

**Attorney Docket No. 8793-52026**

**PATENT**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In Re Application Of: Bellaiche, L., et al.

Appl. No.: 10/632,740

Group Art Unit: 1755

Filed: 08/01/2003

Examiner: Koslow, C.

For: Enhanced Electromechanical Properties in Atomically-Ordered Ferroelectric Alloys

**Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450**

**DECLARATION UNDER 37 CFR 1.132**

Laurent Bellaiche declares as follows:

1. I am one of the joint inventors of the invention described and claimed in the referenced patent application.
2. I am one of the two authors listed in the abstract attached hereto as Exhibit A and entitled, "Composition modulation in Pb(Sc,Nb)O<sub>3</sub> alloys." A printed copy of the abstract was provided to attendees at the conference entitled "Fundamental Physics of Ferroelectrics 2001." The conference was held at Williamsburg Virginia on February 4-7, 2001. The abstract was also published in the AIP Conference Proceedings. Both of these publications occurred more than one year prior to August 8, 2002, the filing date of Provisional Patent Application No. 60/401,995, from which the present application claims priority.

**BEST AVAILABLE COPY**

3. I made an oral presentation to the "Fundamental Physics of Ferroelectrics 2001" conference on February 5, 2001. The presentation, entitled "Composition modulation in  $\text{Pb}(\text{Sc},\text{Nb})\text{O}_3$  alloys" was accompanied by a set of sixteen (16) slides, copies of which are attached hereto as Exhibit B.

4. According to a booklet provided to attendees, my presentation was scheduled for 3:50 pm to 4:25 pm. A copy of this booklet is attached hereto as Exhibit C. This thirty-five (35) minute period included both the presentation itself and a time period for questions from the attendees. To the best of my knowledge and belief, my oral presentation did not exceed the scheduled time period.

5. Prior to the filing date of the present application, printed copies of the slides were not made publicly available.

6. Prior to the filing date of the present application, the slides were not publicly displayed in any manner other than during the oral presentation described above.

7. To the best of my knowledge and belief, my oral presentation was not recorded in any manner, including by audio or video means or by photography.

8. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above-referenced application or any patent issuing thereon.

Date: 12/14/05

  
\_\_\_\_\_  
Laurent Bellaiche

# Fundamental Physics of Ferroelectrics 2001

February 4-7, 2001  
Williamsburg, VA

Proceedings published in *AIP Conference Proceedings*

Organizing Committee:

Henry Krakauer, College of William & Mary  
Haydn Chen, U. of Illinois Urbana-Champaign

Sponsored by

The Office of Naval Research and  
The College of William & Mary



EXHIBIT

A

tabbles

# Composition modulation in $\text{Pb}(\text{Sc},\text{Nb})\text{O}_3$ alloys \*

L. Bellaiche and A.M. George

*Physics Department, University of Arkansas,*

*Fayetteville, Arkansas 72701, USA*

A first-principles-derived approach is used to study properties of  $\text{Pb}(\text{Sc},\text{Nb})\text{O}_3$  alloys that are compositionally modulated along a direction away from the *total* electrical polarization. The direction of the *local* electrical polarizations (centered in the planes perpendicular to the modulation direction) is found to be spatially-dependent, and can be adjusted with the modulation parameters. Furthermore, modulated structures with large composition gradients adopt a new monoclinic phase for their ferroelectric ground state, and exhibit very large piezoelectric and dielectric coefficients. These unusual features can be viewed as a consequence of a composition modulation-induced internal electric field.

\* Supported by ASTA grant N99-B-21, NSF grant DMR-9983678 and ONR grant N00014-00-1-0542.

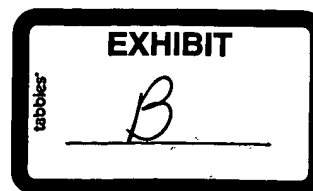
Williamsburg, Feb. 2001

# Composition Modulation in $\text{Pb}(\text{Sc},\text{Nb})\text{O}_3$ Alloys <sup>1</sup>

A.M. George, J. Iniguez and L. Bellaiche

*Physics Department, University of Arkansas*

<sup>1</sup> Supported by ONR N00014-00-1-0542,  
NSF DMR-9983678 and ASTA N99-B-21



## Examples of recent discoveries:

- 1) *High piezoelectricity* in single-crystals of PZN-PT and PMN-PT ( $\sim 2,000$  pC/N)  
[S.-E. Park and T.E. Shtrout, J. Appl. Phys. 82, 1804 (1997)]
- 2) *Monoclinic phase* in the morphotropic phase boundary of PZT  
[B. Noheda *et al*, Appl. Phys. Lett. 74, 2059 (1999)]
- 3) *Asymmetry of the double-well potential* in  $\text{ABO}_3$  /  $\text{AB}'\text{O}_3$  /  $\text{AB}''\text{O}_3$  structures  
[N. Sai *et al*, Phys. Rev. Lett. 84, 5636 (2000)]

Ferroelectric alloys show great promise for the development of new materials

## Aim of the present study:

To look for a *mechanism*:

1. Occurring in ferroelectric alloys
2. Yielding new structural properties.
3. Leading to huge electromechanical responses

—→ This mechanism is the *composition modulation*

## Plan of the talk:

I. Method

II. Composition modulation in  $\text{Pb}(\text{Sc},\text{Nb})\text{O}_3$

III. Understanding the unusual features

## I. Method: Heff for $A(B'_{1-x} B''_x)O_3$

- Mimic the true alloy  $A(B'_{1-x} B''_x)O_3$  by a virtual simple  $A\langle B \rangle O_3$  system

$$\rightarrow E_1(\{\eta\}, \mathbf{u})$$

depends on strain  $\{\eta\}$  and mode  $\mathbf{u}$   
[ Zhong *et al*, PRL 73, 1861 (1994) ]

- Consider alloying as a perturbation of the  $A\langle B \rangle O_3$  system

$$\rightarrow E = E_1(\{\eta\}, \mathbf{u}) + E_2(\{\eta\}, \mathbf{u}, \{\sigma\})$$

Incorporates alloy conf.  $\{\sigma\}$   
[ Bellaiche *et al*, PRL 84, 5427 (2000) ]

- All the parameters of  $E_1$  and  $E_2$  are determined by first-principles calculations

## Expression of $E_2$ in $\text{Pb}(\text{Sc},\text{Nb})\text{O}_3$

$\sigma_j = +1$  : Niobium atom on site  $j$

$\sigma_j = -1$  : Scandium atom on site  $j$

Most important interaction: Intersite effect  
between atom on site  $j$  and local mode on site  $i$

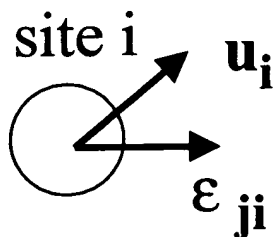
$$E_2 = \sum_i \left( \sum_j Q_{j,i} \sigma_j \mathbf{e}_{ji} \right) \cdot \mathbf{u}_i = - \sum_i \left( \sum_j \epsilon_{ji} \right) \cdot \mathbf{Z}^* \mathbf{u}_i$$

all negative  
(up to 3<sup>rd</sup> nn)

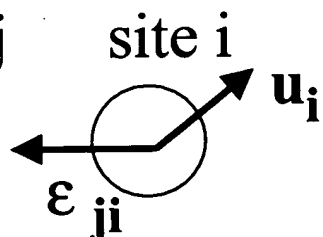
unit vector  
from  $j$  to  $i$

“Electric-field”  
generated by  
atom sitting on  $j$

Nb on site  $j$

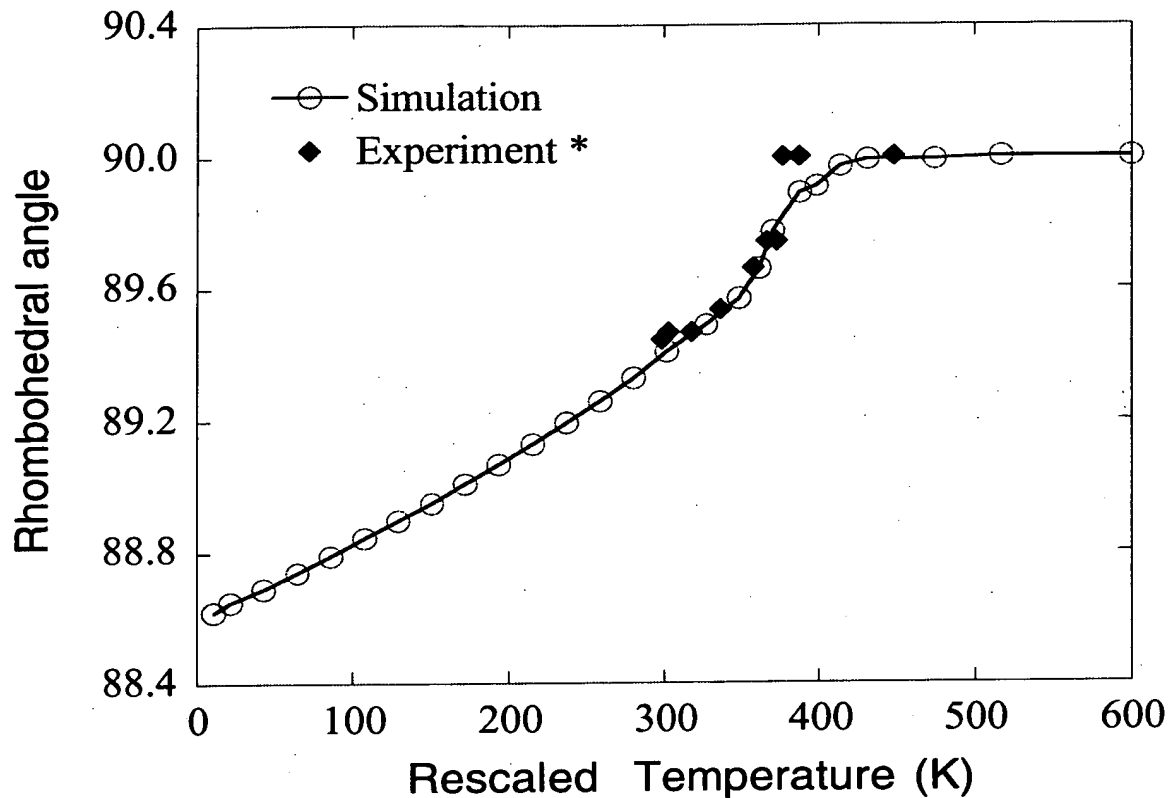


Sc on site  $j$



## Accuracy of $H_{\text{eff}}$ for $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$

### 1. Disordered $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PSN):



Correct phase transition and good agreement with experiment [\* Chu et al, J. Appl. Phys. 77, 1671 (1995)]

### 2. Rocksalt-ordered PSN at small temperature:

$H_{\text{eff}}$   
Rhombohedral with  
 $\langle \mathbf{u} \rangle = 0.0675(\mathbf{x} + \mathbf{y} + \mathbf{z})$

LDA  
Rhombohedral with  
 $\langle \mathbf{u} \rangle = 0.0679(\mathbf{x} + \mathbf{y} + \mathbf{z})$

## II. Composition Modulation in $\text{Pb}(\text{Sc}_{1-x(k)}\text{Nb}_{x(k)})\text{O}_3$

The composition  $x(k)$  varies along  $[001]$

$$x(k) = x_0 + A f(k, \lambda)$$

Integer indexing  
the (001) planes

Average  
composition  
(50 %)

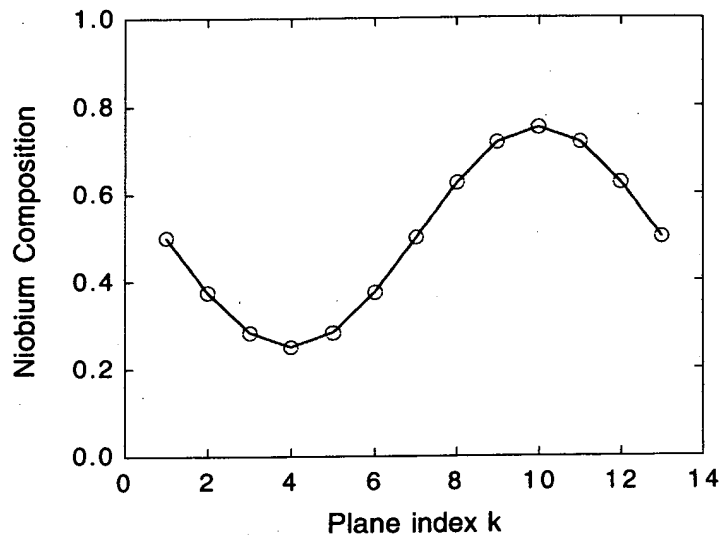
Amplitude

Shape

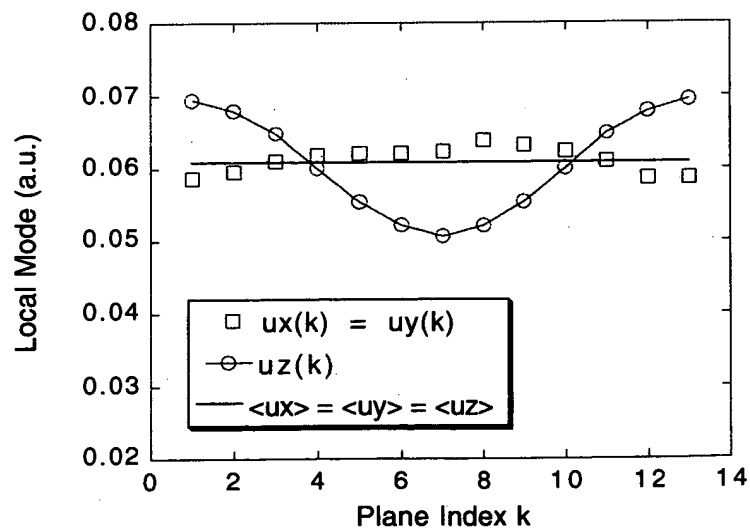
Wavelength

Atomic disorder is assumed in each (001) plane

Sinusoidal modulation with  $A=0.25$  and  $\lambda=12a$

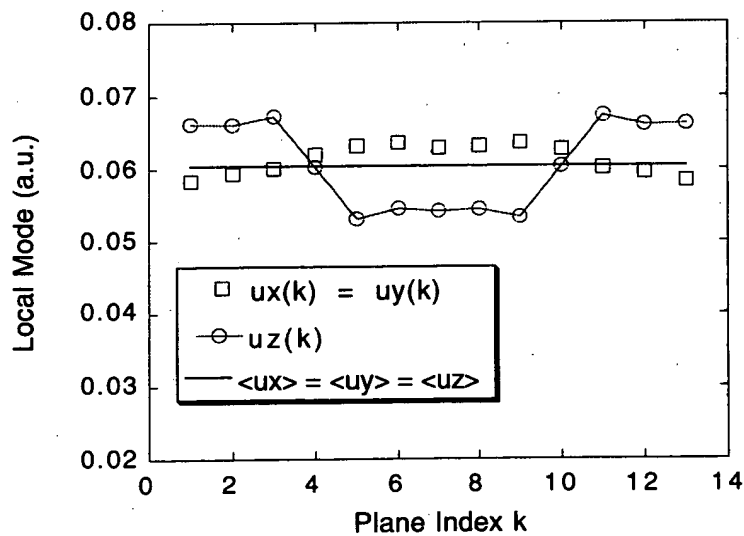
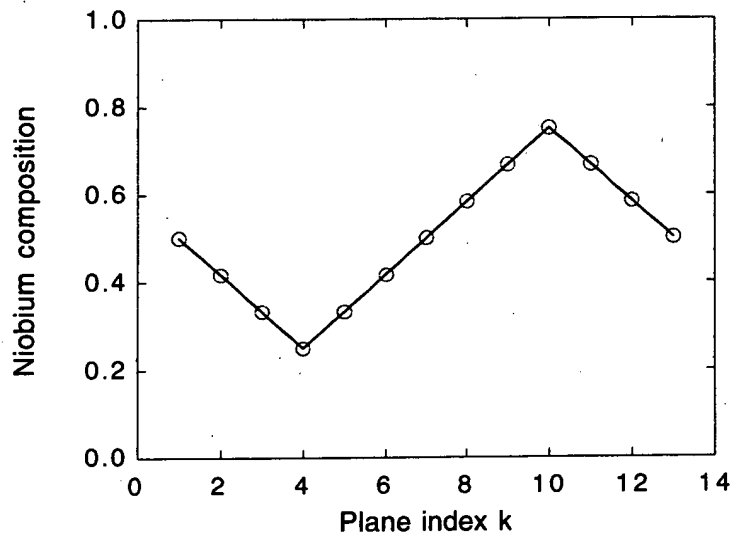


Effect on local modes at 50K



- Rhombohedral ground state (Total  $\mathbf{P} \parallel [111]$ )
- $uz(k)$  sinusoidally varies as a function of  $k$ 
  - Local polarizations are *spatially-dependent*

*Saw* modulation with  $A=0.25$  and  $\lambda=12a$

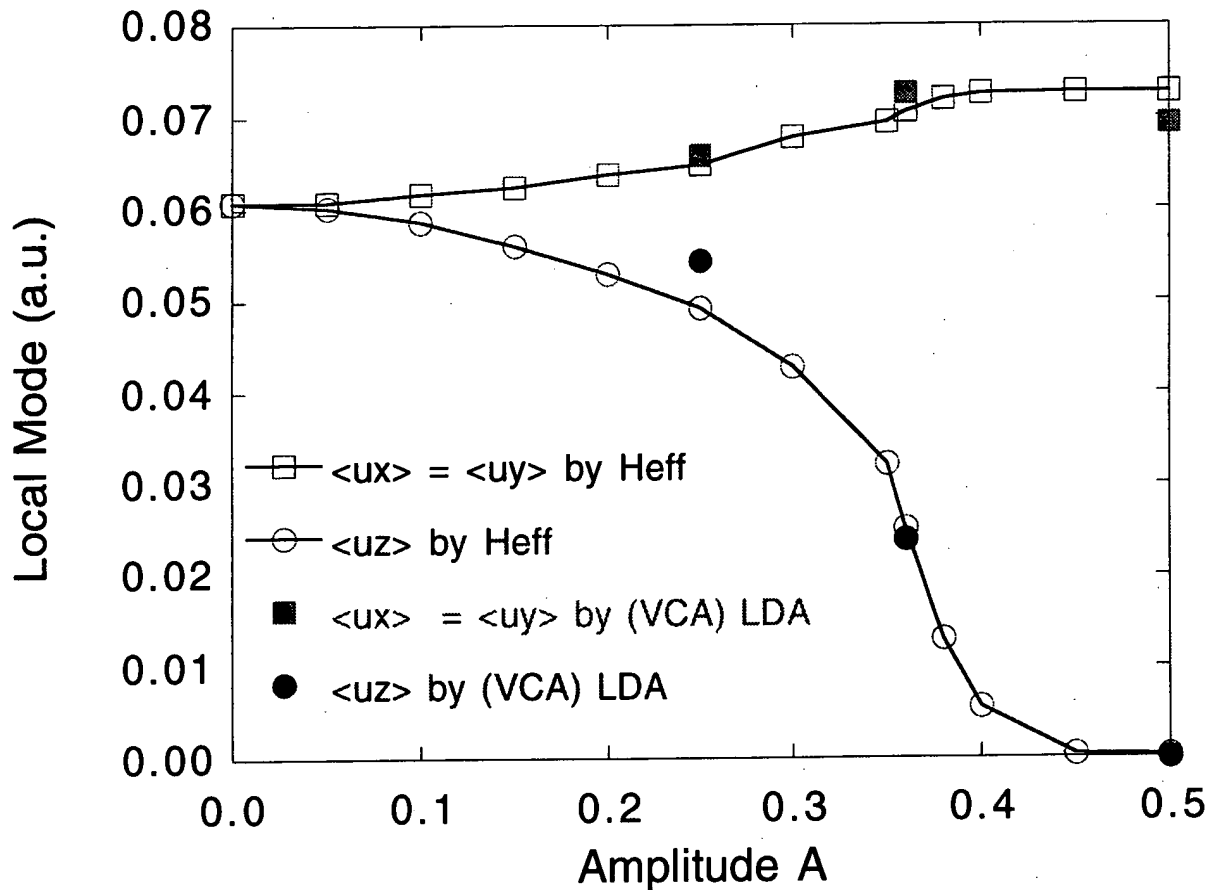


- Rhombohedral ground state
- The local polarizations can be shaped by adjusting the parameters of the modulation

Is it possible to change the ground-state?

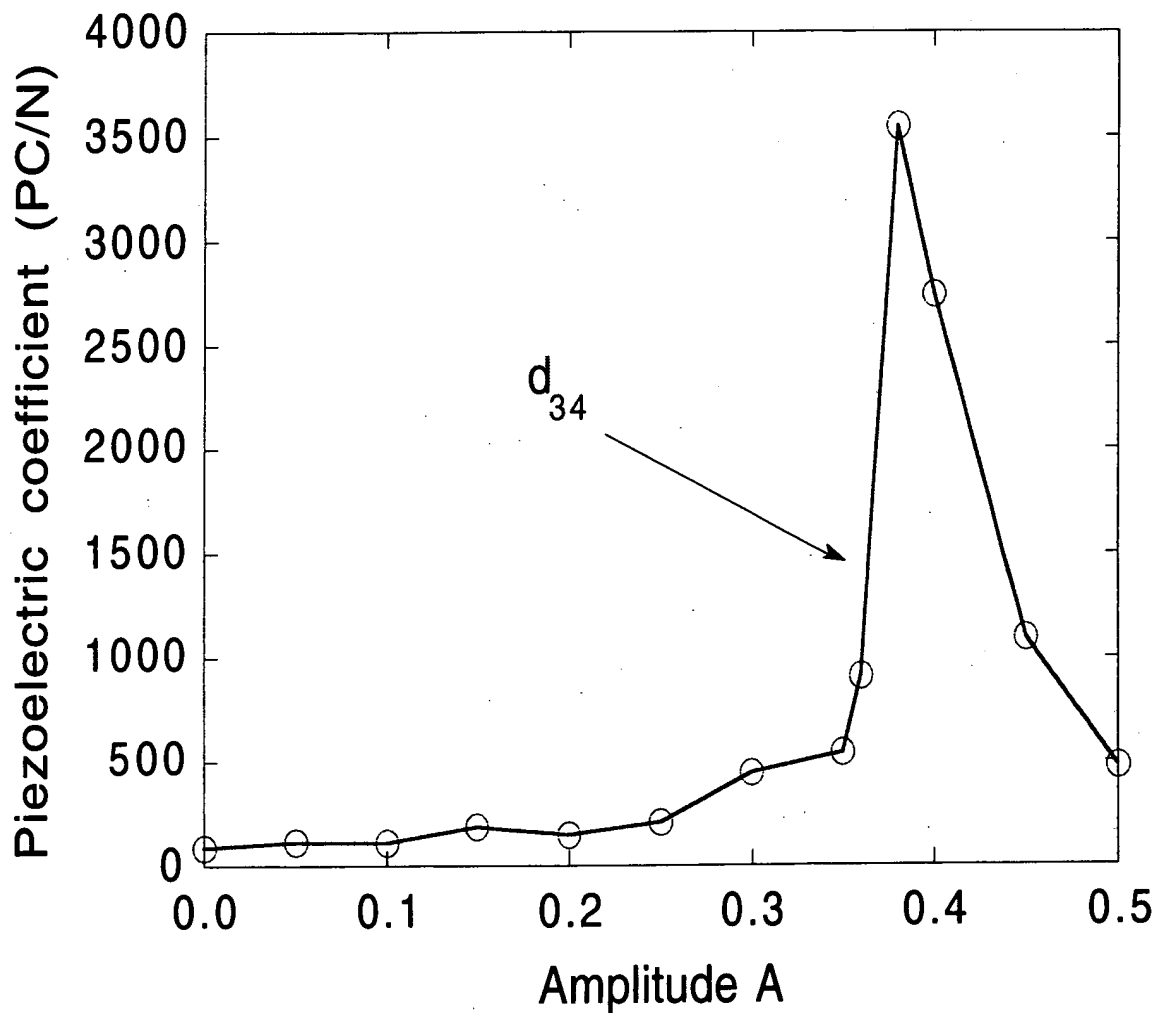
Saw modulation with  $\lambda=4a$  and *tuning*  $A$

$$\frac{(\text{Sc}_{0.5} \text{Nb}_{0.5}) / (\text{Sc}_{0.5+A} \text{Nb}_{0.5-A})}{(\text{Sc}_{0.5} \text{Nb}_{0.5}) / (\text{Sc}_{0.5-A} \text{Nb}_{0.5+A})}$$



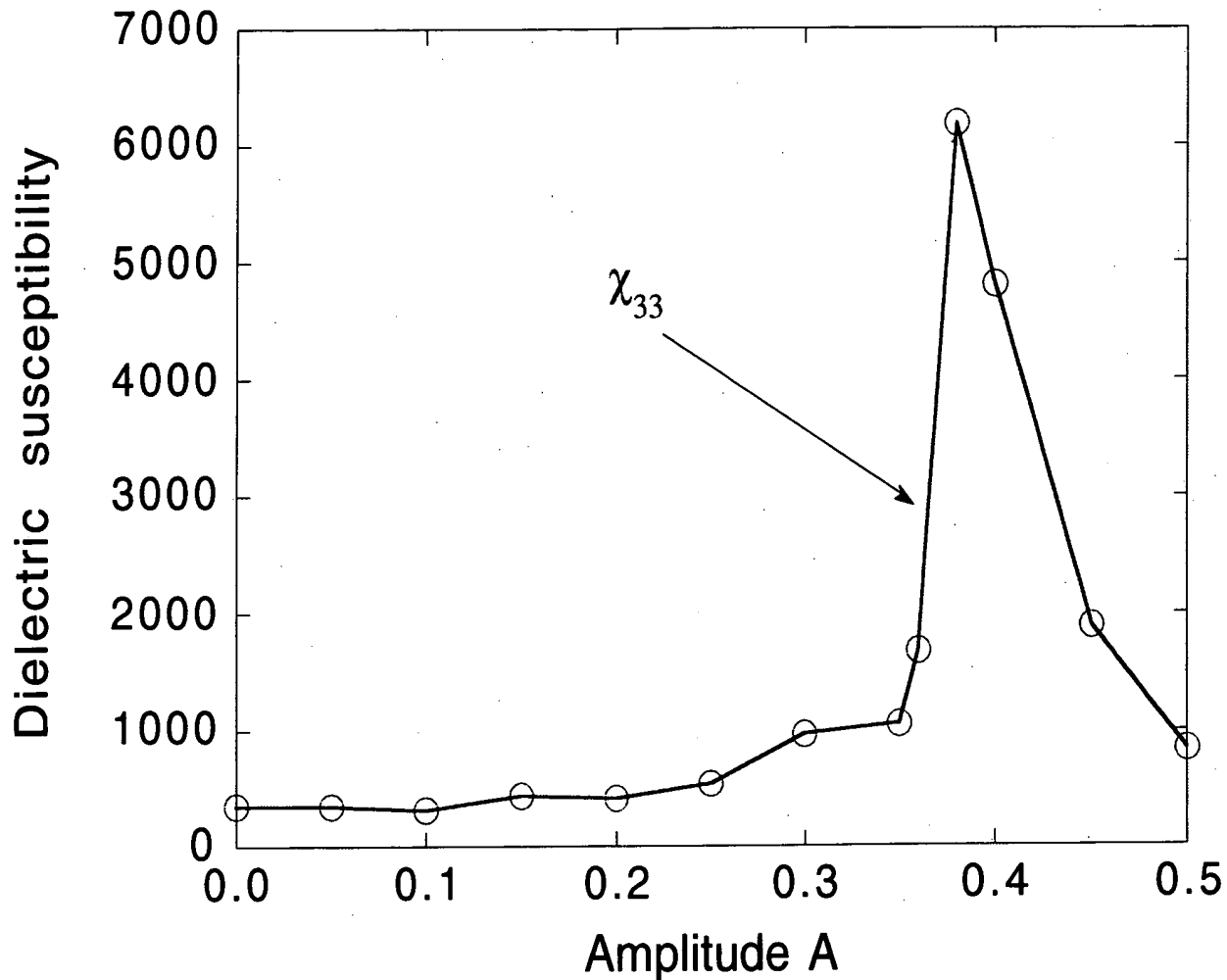
- Rhombohedral phase for small  $A$  ( $\mathbf{P} \parallel [111]$ )
- Monoclinic phase for intermediate values of  $A$   
 $\longrightarrow \mathbf{P}$  between the  $[111]$  and  $[110]$  directions
- Orthorhombic phase for the largest  $A$  ( $\mathbf{P} \parallel [110]$ )

## Effect on piezoelectricity (at 50K)?



Huge shear piezoelectric coefficient!!!  
(around the monoclinic--orthorhombic transition)

## Effect on dielectric response (at 50K)?



Large dielectric susceptibility  
(around the monoclinic--orthorhombic transition)

### III. Understanding the unusual features

Composition modulation generates an internal electric-field along [001], acting on the  $k^{\text{th}}$  plane:

$$\mathbf{E}(k) = g(\{Q_{j,i}\}) [x(k+1) - x(k-1)]$$

↑  
Strongly negative  
in PSN

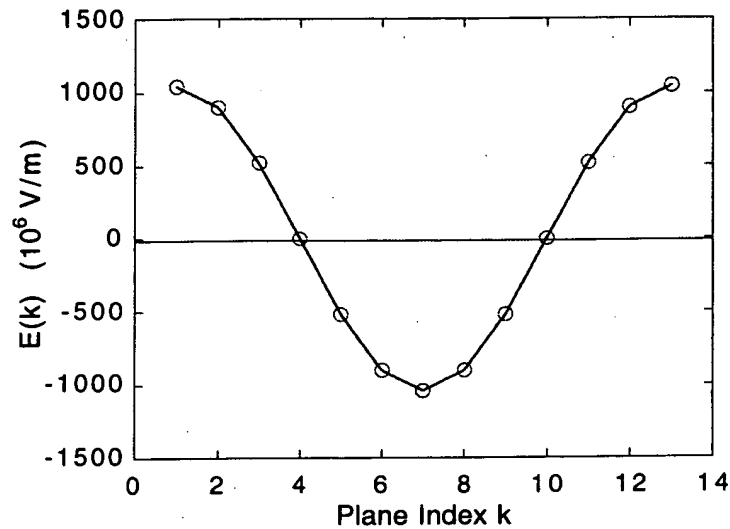
↑  
Modulation parameters  
play a role

$$E(k) < 0 \text{ when } x(k+1) - x(k-1) > 0 \\ \longrightarrow uz(k) < \langle uz \rangle$$

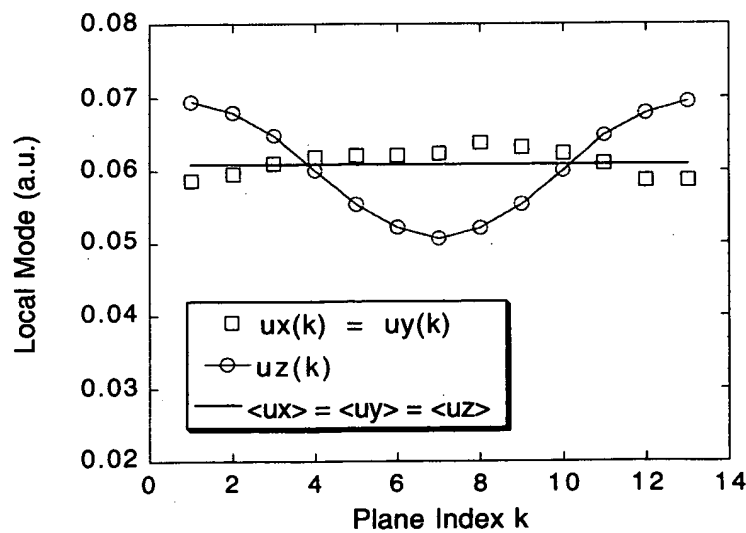
$$E(k) > 0 \text{ when } x(k+1) - x(k-1) < 0 \\ \longrightarrow uz(k) > \langle uz \rangle$$

$$E(k) = 0 \text{ when } x(k+1) - x(k-1) = 0 \\ \longrightarrow uz(k) = \langle uz \rangle$$

Sinusoidal modulation with  $A=0.25$  and  $\lambda=12a$



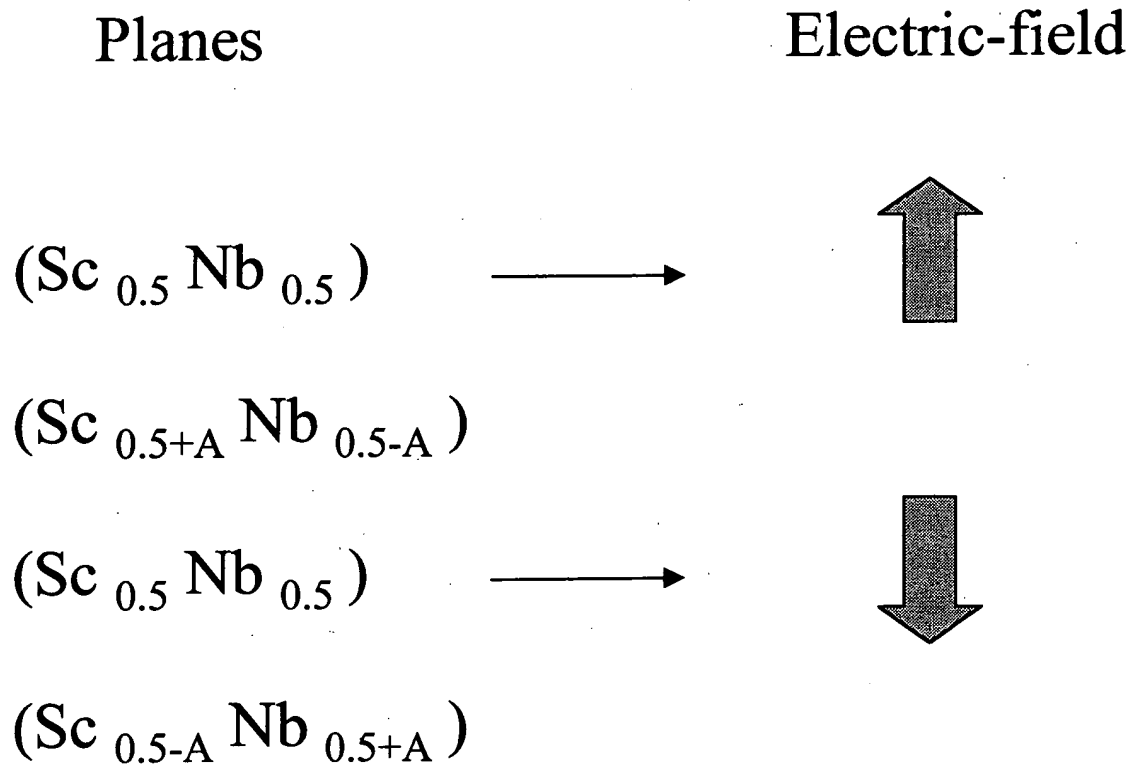
Effect on local modes at 50K



Local polarizations are shaped by the internal electric-field!!!

Why is it possible to alter the ground-state?

Saw modulation with  $\lambda=4a$  and *tuning*  $A$



Magnitude of  $E$  is linearly dependent on  $A$

- $\longrightarrow$   $\langle u_z \rangle$  decreases when increasing  $A$
- $\longrightarrow$  Monoclinic phase for intermediate  $A$
- $\longrightarrow$  Orthorhombic phase for the largest  $A$

# Conclusions

- Use a first-principles derived scheme to study properties of compositionally modulated PSN
- These structures exhibit unusual features
  - Local polarizations that can be shaped by adjusting the modulation parameters
  - New structural phases
  - Large electromechanical responses
- These unusual features result from the existence of an internal electric-field

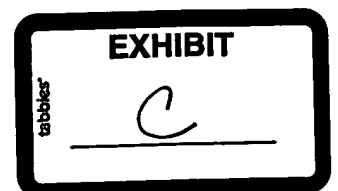
# Fundamental Physics of Ferroelectrics 2001

February 4-7, 2001  
Williamsburg, VA

Proceedings published in *AIP Conference Proceedings*

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# 2001 Workshop on Fundamental Physics of Ferroelectrics

February 4-7, 2001, Williamsburg, VA, USA

## Schedule

Sun Feb 4	5:00 PM	7:00 PM	REGISTRATION	CASCADES FOYER
	5:30 PM	7:00 PM	RECEPTION	COUNCIL ROOM
	7:00 PM		DINNER	COUNCIL ROOM
Mon Feb 5	8:00 AM	8:30 AM	REGISTRATION	CASCADES FOYER
			CASCADES ROOM	Session Chair: Henry Krakauer
	8:30 AM	8:40 AM	Opening Remarks	
	8:40 AM	9:15 AM	J. Scott	Polarons and oxygen vacancy clusters in ferroelectric thin films
	9:15 AM	9:50 AM	R. Ramesh	Polarization dynamics in ferroelectric thin films and nanostructures
	9:50 AM	10:15 AM	COFFEE	
	10:15 AM	10:50 AM	D. Vanderbilt	Domain walls and compositional disorder in Pb-based perovskites
	10:50 AM	11:25 AM	R. Cohen	Polarization rotational, elastic, and electromechanical properties of piezoelectrics
	11:25 AM	12:00 PM	D. Singh	Lattice distortions in $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ alloys near the morphotropic phase boundary
	12:00 PM	1:00 PM	LUNCH	CASCADES GARDEN ROOM
			CASCADES ROOM	Session Chair: Ronald Cohen
	1:00 PM	1:35 PM	W. Dmowski	Local atomic structure of $\text{PbZrO}_3\text{-PbTiO}_3$ near the morphotropic phase boundary
	1:35 PM	2:10 PM	H. Chen	Synchrotron X-ray studies of superlattice ordering in lead magnesium niobate single-crystal doped with 6.25% Ti
	2:10 PM	2:45 PM	S. Kojima	Broadband-Brillouin scattering of relaxor ferroelectric crystals
	2:45 PM	3:15 PM	COFFEE	
	3:15 PM	3:50 PM	K. Rabe	Improving effective Hamiltonians for simple and complex ferroelectric systems
	3:50 PM	4:25 PM	L. Bellaiche	Composition modulation in $\text{Pb}(\text{Sc}, \text{Nb})\text{O}_3$ alloys
	4:25 PM	5:00 PM	K. Bhattacharya	Domain patterns and macroscopic electro-mechanical behavior
	5:00 PM	5:20 PM	GENERAL DISCUSSION	
	6:30 PM	7:30 PM	DINNER	CASCADES GARDEN ROOM
	7:30 PM	9:30 PM	POSTER SESSION	SEMINAR ROOM

## Poster Session, Mon Feb 5, 7:30 PM - 9:30 PM

**R.J. Angel and N.L. Ross**, Characterizing high-pressure phase transitions by X-ray Diffraction

**G. W. Bohannon**, Nonexponential Response in Piezoelectric PVDF

**W. Cao and Ahluwalia**, Computer Simulations of Domain Patterns in Ferroelectrics

**E. Cockayne, B. Burton, and L. Bellaiche**, First-principles Effective Hamiltonians for  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$

**E. V. Colla, Lambert K. Chao, M. B. Weissman**, Multiple Aging Phenomena in Relaxor Ferroelectrics

**N. Dalal and D. Viehland**, Electron-nuclear resonance spectroscopic evidence for defect pinning of microdomains in ferroelectrics: effect of charge and site substitution

**S. Ducharme, T. Reece, A.V. Sorokin, L.M. Blinov, V.M. Fridkin, S.P. Palto, K. Verkhovshaya, N.N. Petukhova, and S.G. Yudin**, Switching dynamics of two-dimensional ferroelectric polymer films

**C.S. Ganpule**, Nanoscale phenomena in ferroelectric thin films

**A. Gruverman**, Ferroelectric domains at nanoscale

**E. Heifets, and R. E. Cohen**, First-Principles and semi-empirical calculations of atomic and electronic structure for  $\text{SrTiO}_3$  (100) and (110) Surfaces

**K. Leung and A. F. Wright**, Properties of PZT 95/5 from first principles

**N.R. Martin, N.J. Ramer, and A.M. Rappe**, Virtual crystal approximation study of monoclinic PZT

**F. C. Marton and R. E. Cohen**, Molecular dynamic simulations of  $\text{MgSiO}_3$

**V. Nagarajan, C. Ganpule, S. P. Alpay, A. Roytburd and R. Ramesh**, Growth and control of domain structure of epitaxial  $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  films grown on vicinal (001)  $\text{SrTiO}_3$ .

**J.B. Neaton and N.W. Ashcroft**, Coexisting electronic and magnetic order in dense oxygen.

**N.J. Ramer, I. Grinberg, and A. Rappe**, Pseudopotential tail norm conservation for ferroelectric modeling

**N. Sai, B. Meyer, and D. Vanderbilt**, Ferroelectric and piezoelectric properties in the presence of compositionally broken inversion symmetry

**M. Suewattana, C. Tahan, P. Larsen, S. Zhang, and H. Krakauer**, Kinetic Monte Carlo simulations of crystal growth in ferroelectric materials

**E.L. Venturini, G.A. Samara, B.A. Tuttle, and V.H. Schmidt**, Pressure Dependence of the Phase Diagram for PZN/PT and PMN/PT Single Crystals

**V. S. Vikhnin, R. I. Eglitis, E.A. Kotomin, and S. Kapphan**, New polaronic-type excitons in ferroelectric oxides: nature and experimental manifestation

**Z. Wu and H. Krakauer**, Charge transfer electrostatic model of compositional order in perovskite alloys

Tue Feb 6 CASCADES ROOM

8:30 AM 9:05 AM B. Burton

9:05 AM 9:40 AM A. Rappe

9:40 AM 10:10 AM COFFEE

10:10 AM 10:45 AM R. Blinc

10:45 AM 11:20 AM Y. Yacoby

11:20 AM 11:55 AM R. Resta

11:55 AM 1:20 PM LUNCH

CASCADES ROOM

1:20 PM 1:55 PM S. Vakhrushev

1:55 PM 2:30 PM D. Viehland

2:30 PM 3:05 PM N. Dalal

3:05 PM 3:35 PM COFFEE

3:35 PM 4:10 PM A. Filippetti

4:10 PM 4:45 PM R. Caracas

7:00 PM 9:00 PM BANQUET

Session Chair: David Vanderbilt

Cation ordering in  $[\text{Na}_{1/2}\text{Bi}_{1/2}]\text{TiO}_3$  alloys

Geometric formulation of quantum stress fields in density functional theory

Dynamics of relaxors

Ferroelectricity in doped incipient ferroelectrics

What happens inside a polarized dielectric?

CASCADES GARDEN ROOM

Session Chair: Shiwei Zhang

Lattice dynamics of PMN measured by inelastic neutron scattering

Importance of quenched-disorder on the structure-property relations of oriented piezocrystals

$^{17}\text{O}$  Isotropic Chemical Shift Probing of Phase Transitions in H-bonded Solids: Squaric Acid

First-Principles study on the coexistence of magnetism and ferroelectricity in  $\text{YMnO}_3$

First-principles study of  $\text{Pb}_2\text{MgTeO}_6$  perovskites

SHIELDS TAVERN, Duke of Gloucester St.

Wed Feb 7 CASCADES ROOM 2

8:30 AM 9:05 AM A. Bussman-Holder

9:05 AM 9:40 AM V. Vikhnin

9:40 AM 10:10 AM COFFEE

10:10 AM 10:45 AM G. Samara

10:45 AM 11:20 AM H. Schmidt

11:20 AM 11:55 AM S. Ducharme

11:55 AM 1:00 PM LUNCH

Session Chair: Takeshi Egami

Why is there a  $T_c$  isotope effect in  $\text{KH}_2\text{PO}_4$  upon deuteration but not when replacing  $^{16}\text{O}$  by  $^{18}\text{O}$ ?

Model of polar clusters in relaxors: charge transfer and local configuration instability effects

Pressure as a probe of ferroelectric properties: quantum regime

Bound charge diffusion and polar nanocluster dynamics in proton glass crystals

Pyroelectric scanning microscopy of ferroelectric polymer films

CASCADES GARDEN ROOM

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# Polarons and Oxygen Vacancy Clusters in Ferroelectric Thin Films: Vacancy Self-patterning and "Fatigue as a Phase Transition"

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We have carried out infrared absorption studies of polarons in both lead zirconate titanate (PZT) and barium-strontium titanate (BST) as functions of temperature (20 - 650 K), donor and acceptor doping, fatigue, and carrier concentration. The random fields associated with Ba/Sr occupancy in BST or Zr/Ti site occupancy in PZT facilitate Anderson localization. Oxygen vacancies order in [1D] chains and/or [2D] rafts. Anderson localization in dimensions less than [3D] have a zero-field threshold. Thus, strong polaron localization is expected in such ferroelectric films. In agreement with this we find strong polaron absorption in BST and PZT near 4000 cm<sup>-1</sup> but not in pure strontium titanate or SBT (strontium bismuth tantalate). The polaron mass  $M^{**}$  is found to be  $16 m(\text{elec.}) = 3 M^{*}$  (band mass). This may affect transport and leakage current models. Second harmonic generation is nominally forbidden in BST and SrTiO<sub>3</sub> but occurs strongly. Its temperature dependence (increasing by x5 from ambient to 4 K) gives a measure of oxygen vacancy cluster size and is fitted to the detailed theory of Prosandeev; this is a no-free-parameter fit, with the constants obtained independently from the temperature at which the reciprocal dielectric constant extrapolates to zero from above (36±3 K) and the lowest symmetric q=0 phonon energy at 4 K (ca. 40 cm<sup>-1</sup>). The results are related to the concept of "fatigue as a percolative phase transition", and it is found that Steinsvik's oxygen vacancy activation enthalpy  $H$  in strontium titanate varies near a critical concentration of  $X_c = 7\%$  as

$$H(x) = (X_c - x)^g$$

where  $g = 7/4$  is the percolation exponent for a cubic lattice. At  $X_c = 7\%$  a phase transition to a 2x2x1 superlattice occurs. The oxygen vacancies order along [101] axes according to Becerro et al.; this is the axis of the main domain walls involved in pinning and fatigue (Janovec, private communication) as observed by McKinstry, Randall, et al. in PZT.

POLARIZATION DYNAMICS IN FERROELECTRIC THIN FILMS AND NANOSTRUCTURES  
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Over the past several years, there has been considerable focus on ferroelectric thin films, specifically for possible use in nonvolatile memories. A significant portion of the work to date has focused on thin film processing, process integration and reliability studies, specifically approaches to solving the problems of fatigue and imprint. However, in order for thin films of PZT and SBT (the two primary materials systems under consideration) to be successfully implemented in nonvolatile memories, several other basic and applied problems have to be resolved. Specifically, the switching dynamics of the spontaneous polarization under applied field; the long term relaxation of the remanent polarization state and the scaling of the ferroelectric properties with lateral and vertical dimensions are issues of a fundamental nature and require rigorous understanding. From another point of view, ferroelectric and dielectric perovskites present very fascinating systems where the dynamics of the spontaneous polarization or that of dipolar clusters over the time scale of 1psecond to 10 years (almost 20 decades of time) is of great relevance from both the fundamental and applications point of view. The use of novel surface probes such as electric force microscopy, scanning capacitance microscopy is now enabling high resolution studies of the ferroelectric and dielectric properties. In this presentation, I will present results of studies aimed at understanding the interplay between thin film processing, size effects, film microstructure and polarization dynamics (specifically relaxation dynamics). Sub-micron ferroelectric capacitors have been fabricated by focused ion beam milling and are being probed using a combination of conventional characterization techniques as well as novel surface probes such as scanned force microscopy and spectroscopy. This approach has enabled us to image polarization relaxation phenomena at a resolution of 20nm ; these measurements coupled with theoretical treatments have revealed the details of nucleation and growth of reverse domains. We have been able to directly measure the ferroelectric and piezoelectric properties of sub-100nm capacitors. In such sub-micron structures we find that the polarization dynamics of 90=B0 domain walls is very different from continuous films. Specifically, we find that by releasing the clamping effects imposed by the substrate through focused ion beam milling, 90=B0 domain walls can be moved by the application of an electric field. This observation is of critical importance in enabling approaches that can take advantage of the large (4%) strain that is generated by the movement of the 90=B0 domain wall. We have also found that we can control the location and the polarization direction within the 90=B0 domain through the use of vicinally cut substrates. The results of these experiments point to approaches to create novel, electrically tunable ferroelectric gratings.

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## Domain Walls and Compositional Disorder in Pb-based Perovskites

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Two aspects of recent work on the properties of Pb-based ferroelectric perovskites will be discussed. First, a thorough understanding of ferroelectric switching requires a microscopic description of the underlying domain walls and their dynamics. We have carried out ab-initio calculations of 90° and 180° ferroelectric domain walls in PbTiO<sub>3</sub>. We find that it is possible to construct metastable supercell structures representing both kinds of domain walls using supercells of only modest size. The relaxed structure, energy, and polarization profile are calculated for each case. Two features of the 90° dislocation are surprising: the barrier for its motion is found to be miniscule, and a small offset of the electrostatic potential across the domain wall is found. Second, a first-principles-derived approach is used to study the properties of rocksalt-ordered and disordered Pb(Sc<sub>0.5</sub>Nb<sub>0.5</sub>)O<sub>3</sub> (PSN) alloys [1]. The paraelectric-to-ferroelectric transition temperature  $T_c$  is strongly dependent on the atomic configuration, while the piezoelectric response *vs.*  $T/T_c$  is nearly independent of the chemical order. Our calculations are consistent with the experimental finding [2] that, at  $T = T_c$ , ordered PSN undergoes a normal ferroelectric transition, while disordered PSN transforms from a relaxor state to a ferroelectric state.

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## **Polarization Rotational, Elastic, and Electromechanical Properties of Piezoelectrics**

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Macroscopic polarization in crystals is a vector quantity that is a bulk property, and the conventional picture of maximum coupling to electric fields was to apply an electric field parallel to the polarization to induce a strain, in order to maximum the coupling between the electric field and polarization vectors. However, the electromechanical response is governed by the piezoelectric constants, which are third-rank tensors, and in general are not required to give a maximum strain when the polarization and applied field are parallel. Fu and Cohen [1] proposed that this effect is responsible for the huge piezoelectric response found in PZN-PT and PMN-PT piezoelectrics [2] through polarization rotation. This apparently has become quickly accepted, and new experimental data supports this idea. For example, an intermediate monoclinic phase has been discovered in PZT between the rhombohedral and tetragonal phases [3], that is understood as the rotation of the polarization from (111) to (001), so apparently polarization rotation even occurs in the absence of an applied electric field. The idea is very simple: rhombohedral perovskite ferroelectrics (e.g. the ground state of  $\text{BaTiO}_3$ ) have a small strain, whereas the lattice strain is much larger in tetragonal ferroelectric perovskites (1% in  $\text{BaTiO}_3$  and 6% in  $\text{PbTiO}_3$ , for example). By applying a field along (001), oblique to the (111) rhombohedral polarization, one can obtain a huge strain as the polarization is rotated to (001). This can also be thought of as a field induced phase transition from rhombohedral to tetragonal, through an intermediate monoclinic phase. In some cases this may be a continuous transition, and in other cases there may be a first-order transition at some applied field, and thus hysteresis and a discontinuity in strain with field.

The computation of macroscopic polarization using the Berry's phase approach [4] is the key to a first-principles understanding of piezoelectricity. We have used the Linearized Augmented Plane Wave (LAPW) method within the LDA and GGA to compute the piezoelectrics constants of  $\text{PbTiO}_3$  and PZT 50/50 [5]. For  $\text{PbTiO}_3$  we find good agreement with experiment, though there is a wide spread among experimental measurements. There are three pieces to understanding electromechanical response, piezoelectric constants, elastic constants, and dielectric constants. We are now studying the elastic properties of PZT, which should be useful since PZT single crystals have not been successfully grown, so single crystal constants are not directly accessible experimentally.

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## Lattice Distortions in $\text{Pb}(\text{Zr,Ti})\text{O}_3$ Alloys Near the Morphotropic Phase Boundary

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First principles calculations within the framework of density functional theory have shown that both ferroelectric distortions that provide piezoelectric couplings and instabilities consisting of octahedral rotations are close in energy over a wide range of compositions in the rhombohedral part of the  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  phase diagram. Additionally, based on the opposite pressure dependencies of these two basic instabilities, it has been suggested that they may coexist locally near the morphotropic phase boundary. This is due to the coupling to local strain fields arising from the B-site cation disorder. Here we review these results and present details of first principles structural relaxations for supercells with a variety of local Zr-Ti orderings. These are to show this effect, as well as to elucidate the Pb displacements for various local chemical environments in the disordered  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  alloy. The results are discussed in terms of the Pb-O chemistry, particularly hybridization of Pb states with O *p* states and the interplay between displacive and rotational instabilities, particularly the fact that variations in the amplitude of the ferroelectric instability can occur on shorter length scales than that of rotational instabilities in  $\text{Pb}(\text{Zr,Ti})\text{O}_3$ .

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"Local atomic structure of  $\text{PbZrO}_3\text{-PbTiO}_3$  near the morphotropic phase boundary".

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We have studied the local atomic structure of  $\text{PbZrO}_3\text{-PbTiO}_3$  solid solution (PZT) near the morphotropic phase boundary (MPB) using pulsed neutron scattering. PZT is applied as solid state sensors and actuators that couple strain to electric signal. On the Zr-rich side PZT is antiferroelectric and has the orthorhombic  $\text{Pbam}$  structure up to 7% of  $\text{PbTiO}_3$ , while above 7% it becomes ferroelectric with the rhombohedral structure. The PZT phase diagram is characterized by the almost vertical MPB [1] at 48-52% of PT, which separates the Zr rich rhombohedral phase from the tetragonal ( $\text{P4mm}$ ) Ti rich phase. At this phase boundary the piezoelectric response of PZT is exceptionally high and stable over a wide range of temperature. Recently a high resolution x-ray diffraction study of PZT at the MPB at low temperatures revealed a previously unknown monoclinic phase  $\text{Cm}$  [2]. However, it is difficult to determine local atomic displacements away from the high symmetry positions from the crystallographic studies. In our study, in addition to conventional crystallographic Rietveld analysis, we used the pair distribution function (PDF) method. Since the PDF is obtained by the direct Fourier-transformation of both the Bragg peaks and diffuse scattering intensity the inter-atomic distances are obtained without the assumption of the unit cell symmetry. While the crystal structure changes substantially through the MPB, we found that the local atomic structure does not show dramatic changes. The actual change is more of a statistical nature in the population of Pb displacements. Crystallographically the Pb displacement is in  $[100]$  in the tetragonal phase and  $[111]$  in the rhombohedral phase, with the rotation from one to the other in the intermediate monoclinic phase. Locally, however, pure  $[111]$  Pb displacements are not observed even in the Zr-rich rhombohedral phase. The  $[100]$  displacements are majority in the tetragonal phase, while they are gradually replaced by the  $[110]$  displacements through the MPB. The distortions of the Ti and Zr oxygen octahedra are very close to those observed in pure PT and PZ. The observed gradual change in the local structure through the MPB suggests that the "polarization rotation" is driven by the gradual change in the partition of the Pb displacement patterns, and the crystal structure simply reflects the change in the average structure.

# Synchrotron X-ray Studies of Superlattice Ordering in Lead Magnesium Niobate Single Crystal Doped with 6.25% Ti

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## Abstract

Temperature dependence of the correlated displacements in small regions of approximately 30 Å has been studied in the lead magnesium niobate (PMN) single crystal containing 6.25 % Ti (PMN-PT), using synchrotron x-ray scattering techniques. Local phase transition temperature has been found by monitoring superlattice reflections located at the face-centered locations in the reciprocal space, known as  $\alpha$  spots. These superlattice reflections are related to the atomic displacements, which are correlated on the short-range scale in the nanoregions that are different from the chemical nanodomains. Displacements are believed to be anti-ferrodistortive in nature and their magnitude decreases with increasing temperature below the freezing temperature,  $T_f \sim 260$  K, while the radius of these nanoregions was found to be temperature independent.  $T_f \approx 260$  K, that marks the local structural phase transition in the nanoregions, is very close to the phenomenological freezing temperature, obtained from the Vogel-Fulcher fit to the frequency dependence of the dielectric response for this particular composition. A comparison of PMN-PT results to the pure PMN, where nanodomains due to both anti-ferrodistortions and chemical ordering were found, will be presented. Structure-property relationship in the relaxor systems will be also discussed.

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## Broadband-Brillouin Scattering of Relaxor Ferroelectric Crystals

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The fast relaxation process of relaxor ferroelectric crystals is studied by broadband-Brillouin scattering technique. The quasielastic scattering appears at about 100K above the cubic to tetragonal transition temperature  $T_{ct}$  in a PMN-PT crystal. On further cooling its intensity increases down to  $T_{ct}$ . Since the spectral resolution is very high, the relaxation time is determined accurately as a function of temperature. Consequently, the fast relaxation in GHz region is clearly observed. Similar quasielastic scattering is also observed in PZN-PT and SBN crystals. The change of sound velocity and damping is also observed above  $T_{ct}$ . By combining a microscope with a Fabry-Perot Interferometer, the position dependence of elastic properties is also studied by changing the spot area to be observed.

## Improving effective Hamiltonians for simple and complex ferroelectric systems

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First-principles effective Hamiltonians have proved generally quite successful in simulating the finite-temperature structure and properties of ferroelectrics and related materials. However, there are quantitative discrepancies with experimental results, especially in transition temperatures. These are in part due to the use of approximate density functionals and to idealization of the real systems, and in part due to the additional approximations associated with the effective Hamiltonian approach. In this talk, I will discuss a number of issues relevant to the latter, including choice of optimal prototype structure, the construction of improved lattice Wannier functions, relaxations in solid solutions and thin films, high-accuracy computation of the quadratic part of the effective Hamiltonian, and higher-order anharmonic terms such as the scaling of interatomic force constants with distance. Examples will be drawn from the ferroelectric semiconductor GeTe, bulk and thin film !  $\text{PbTiO}_3$ , and PZT.

# Composition modulation in $\text{Pb}(\text{Sc,Nb})\text{O}_3$ alloys \*

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A first-principles-derived approach is used to study properties of  $\text{Pb}(\text{Sc,Nb})\text{O}_3$  alloys that are compositionally modulated along a direction away from the *total* electrical polarization. The direction of the *local* electrical polarizations (centered in the planes perpendicular to the modulation direction) is found to be spatially-dependent, and can be adjusted with the modulation parameters. Furthermore, modulated structures with large composition gradients adopt a new monoclinic phase for their ferroelectric ground state, and exhibit very large piezoelectric and dielectric coefficients. These unusual features can be viewed as a consequence of a composition modulation-induced internal electric field.

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## Domain patterns and macroscopic electro-mechanical behavior

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We report on our recent theoretical and experimental work on understanding the electromechanical behavior of ferroelectrics, with particular attention to link between macroscopic properties and domain patterns. We develop a continuum theory based on energy minimization, similar to the classical Landau-Devonshire theory, and use it to understand the domain patterns in single crystals, polycrystals and thin films. We study the effect of applied stress and electric field, and use the theory to find an electro-mechanical loading path that yields large electrostriction. We validate these results experimentally by demonstrating strains close to 1% in  $\text{BaTiO}_3$  single crystals under constant mechanical compression and cycling electric field. In-situ microscopy shows that strains are generated by domain switching mediated by domain wall propagation. We conclude with some recent theoretical results on polycrystals: (i) why it easier to pole PZT near the morphotropic phase boundary and (ii) the effect of texture on electrostriction in thin films.

## B.P. BURTON and E. COCKAYNE

The Vienna Ab-initio Simulation Package (VASP) was used to perform fully relaxed planewave pseudopotential calculations of formation energies ( $\Delta E_{VASP}$ ) for a large number of ordered supercells in the perovskite based system  $NaTiO_3 - BiTiO_3$ ; including 30 supercells at the  $[Na_{1/2}Bi_{1/2}]TiO_3$  composition. From the set,  $\{\Delta E_{VASP}\}$ , the lowest energy configuration, and presumed ground state (GS) is a 40 atom supercell (40GS?) with space group symmetry  $P4_2/mmc$  (neglecting ferroelastic distortions). Its structure is characterized by pseudocubic doubling of the primitive perovskite cell, plus alternating [100] rows of Na and Bi atoms in (hk0) planes and alternating [010] rows in  $(hk\frac{1}{2})$  planes:

$$(000) \qquad (00\frac{1}{2}) \qquad (001)$$

One expects this structure to be easily disordered because  $[\frac{1}{2}00]$  or  $[0\frac{1}{2}0]$  stacking faults can be introduced without changing any cation-cation pair correlations for pairs closer than fourth nearest neighbors. Accordingly, it is no surprise that  $\Delta E_{VAP}^{GS40?} = 163.17$  kJ/ABO<sub>3</sub>, is almost identical to that for an 80-atom supercell,  $\Delta E_{VAP} = 163.02$  kJ/ABO<sub>3</sub>, which is related to GS40? by a  $[\frac{1}{2}00]$  stacking fault, and doubling of the c-axis.

1

# Geometric Formulation of Quantum Stress Fields in Density Functional Theory

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The quantum-mechanical stress is a fundamentally important quantity which provides insight into the relationship between the electronic structure and the mechanical properties of condensed-matter systems. Nielsen and Martin have provided a tractable and well-defined expression of the macroscopic or total stress for periodic solid-state systems within the framework of density functional theory (DFT), allowing the study and prediction of a large class of structural properties from first principles.

The quantum stress field provides significantly more information than the total stress, allowing one to study the spatial dependence of the stress and its relationship with local electronic and structural phenomena. In particular, the quantum stress field can provide new insights into the polarization and piezoelectricity of perovskites. However, previous derivations of the quantum stress field are not unique since they are determined only up to a gauge term.

We will present a unique expression for the quantum stress field within the local density approximation (LDA). Our formulation exploits a known relationship between the strain tensor field and the Riemann metric tensor, giving rise to a quantity which is gauge invariant with respect to choice of energy density. Stress field results from DFT-LDA calculations of solid molecular hydrogen will be reported. Extensions of the formalism to pseudopotentials and gradient corrected exchange-correlation functionals will be discussed.

## Dynamics of Relaxors

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Relaxor ferroelectrics are characterized by a high value of the static dielectric constant and a strong frequency dispersion of the complex dielectric permittivity. In analogy with dipolar glasses the longest relaxation time diverges at a freezing temperature  $T_f$ . It is now generally accepted that the properties of relaxors are due to nanosized polar clusters. We have proposed a spherical random bond - random field (SRBRF) model, which is capable of explaining a number of static properties of relaxors. The basic reorientable dipoles in relaxors are polar clusters, which vary in size and orientation. In view of that the pseudo spin which is proportional to the dipole moment of the polar cluster is not a fixed length vector as in dipolar glasses, but can be regarded as a continuous variable subject only to the spherical constraint. Here we present a dynamical SRBRF model based on the interacting polar cluster picture. We assume that the reorientation of polar clusters is the leading relaxation mechanism above the freezing temperature. The Langevin equations of motion for the polar cluster pseudo spins are written down and an exact stationary solution is obtained in the asymptotic time limit from which the linear and non-linear dielectric permittivities are obtained. The theoretical predictions are compared with experimental results and a theoretical pressure-temperature phase diagram of relaxors is proposed.

# Ferroelectricity in doped incipient ferroelectrics.

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## **Abstract.**

We present a comprehensive model of ferroelectricity in incipient ferroelectrics doped with ferroelectric ions such as  $\text{KTaO}_3\text{:Nb}$ . We show that a strong electron - longitudinal phonon interaction at the impurity sites together with the presence of virtual electrons in the conduction band of the host lattice are responsible for the spontaneous off-center displacements of the impurity ions in the cubic phase. The interaction of these off-center displacements with the host lattice soft mode drives the ferroelectric phase transition. We show that taking the tunneling of the off-center ions into account we can predict quantitatively the critical impurity concentration for  $T_c=0$ , the concentration dependence of  $T_c$ , the temperature dependence of the dielectric constant and the temperature dependence of the soft mode. Finally, taking spin-spin correlations into account we find that the system has a central peak very close to  $T_c$  and the soft mode saturates at a finite value of a few  $\text{cm}^{-1}$ .

## What happens inside a polarized dielectric?

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We address the very basic issue of what happens, at a microscopic level, inside a polarized dielectric. We show that the complete information about electronic polarization is embedded in the microscopic polarization  $\mathbf{P}_{\text{ind}}(\mathbf{r})$ . In a crystalline dielectric this vector field is defined by its Fourier coefficients  $\mathbf{P}_{\mathbf{G}}$ . Previous studies in the literature have addressed the induced electronic *charge* density (alias the divergence of our vector field) where the most relevant information is obliterated. In fact, the coefficients of the induced charge are  $i\mathbf{G} \cdot \mathbf{P}_{\mathbf{G}}$ , while the macroscopic polarization is simply the  $\mathbf{G}=0$  coefficient  $\mathbf{P}_0$ . This shows once more that macroscopic polarization has *nothing to do* with the periodic charge of the polarized dielectric: such fact goes against a common belief, shared by many textbooks, and based on the Clausius-Mossotti model.

We provide a quantum-mechanical expression for  $\mathbf{P}_{\text{ind}}(\mathbf{r})$ , and we present first-principle results for two case studies: an ionic crystal (NaBr), and a covalent one (Si). The vector field has the dimensions of a dipole per unit volume: we don't find, however, useful to visualize it as a "dipole density", thinking in terms of a continuous distribution of dipoles. Instead, the physical meaning of  $\mathbf{P}^{(\text{ind})}(\mathbf{r})$  is better understood by imagining that the applied field is adiabatically switched on in time:  $\mathbf{P}^{(\text{ind})}(\mathbf{r})$  is then proportional to the microscopic current flowing through the sample while the field is switched on and the dielectric is polarized. In a Clausius-Mossotti model such transient current does not cross the cell boundaries, whereas in a real crystal it percolates through the sample. We show that our case studies are both far from the Clausius-Mossotti limit. In the case of Si, the (unperturbed) valence charge defines a continuous network of bonds. When a field is switched on, most of the polarization current  $\mathbf{P}_{\text{ind}}(\mathbf{r})$  flows within narrow channels along the bonds, and steers to keep clear of the core regions: the dominant feature is that the current percolates across the material. Although less dominant, a similar feature occurs even in NaBr: a big surprise, since ionic crystals are usually regarded as prototypical Clausius-Mossotti materials.

For ferroelectrics, which are mixed ionic/covalent materials, we expect a dominant role of percolating transient currents. The present viewpoint is likely to provide a thorough microscopic understanding of the main trends (i.e. high or low polarizability) in different materials.

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## **Lattice dynamics of PMN measured by inelastic neutron scattering.**

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Despite long history of study the details of lattice dynamics of the relaxor ferroelectrics remain unclear. There are still hot discussions in the literature about the origin of the Raman spectra in the relaxors [1]. Recently performed neutron inelastic scattering measurements revealed the soft excitation [2] and disappearance of the low TO mode at small  $q$  [3]. To get a "complete" picture of the phonon dispersion curves in the model relaxor crystal PMN inelastic neutron scattering measurements for energy transfer up to 25 THz were carried out at 12K (to reduce usual anharmonic multiphonon processes) for main high-symmetry directions and lattice-dynamical shell-model calculations were performed. Obtained results are much more complicated than those observed in simple perovskites. There are 4 branches in [100] direction with well defined polarization at small  $q$ , below 6.5 THz a broad unresolved continuum between 6.5 and 12 THz, well defined excitation at 13.4 THz observed at conditions favorable for the observations of longitudinal as well as transverse phonons, and the weak broad signals above 16THz. 6.5 to 12 THz band was observed in longitudinal and transverse geometries and in many Brillouin Zones (BZ), but we were not able to discover any trend such as to follow a strong signal throughout one BZ. Low energy excitations were fitted to the shell model for the virtual crystal with B cation having the mass equal to  $1/3 m_{\text{Mg}} + 2/3 m_{\text{Nb}}$ . No calculated counterpart was found for the 13.4 THz excitation. Some possible ideas to explain the observed results will be discussed.

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## **Importance of quenched-disorder upon the structure-property relations of oriented piezocrystals**

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Investigations of oriented PMN-PT crystals have been performed by various methods. The results have demonstrated the importance of quenched disorder upon the unique properties of these materials. Several important features have been found these are: (i) the observation of a significant ferroelastic switching under uniaxial stress; (ii) various intermediate metastable conditions; (iii) the breakdown of uniform polarization under continuous unipolar excitation; and (iv) the observation of polarization relaxational dynamics which scale with the Random-field theory under bipolar drive during polarization reversal. These data are explained using the concept of symmetry adaptive ferroelectric mesostates. Various symmetry adaptive states exist including monoclinic and orthorhombic, between the stable rhombohedral and tetragonal phases. Symmetry adaptation occurs due to accomodation of the large transformational strain.

## **$^{17}\text{O}$ Isotropic Chemical Shift Probing of Phase Transitions in Hydrogen-bonded Solids: Squaric Acid**

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O-H $\cdots$ O and N-H $\cdots$ O type bonds are known to be involved in ferroelectric phase transitions and other cooperative phenomena shown by a variety of solids, but the underlying mechanisms is not yet well understood. Current theoretical models assume relatively little or no role for the O atom, but this is perhaps related to the lack of suitable experimental data, in particular that obtainable by high resolution NMR. Here we present our  $^{17}\text{O}$  MAS results on squaric acid,  $\text{H}_2\text{C}_4\text{O}_4$ , through its paraelectric-antiferroelectric phase transition at 100°C. The data clearly demonstrates that MAS using single crystals provides much ( $\sim$ factor of 4) narrower peaks than with powders, pointing to the role of the anisotropic bulk magnetic susceptibility (ABS) broadening mechanisms [Klymachyov and Dalal, *Z. Phys. B* 104, 651, 1997), Fu et al., *J. Phys. Chem.* 102, 8732 (1998)]. The spectrum consists of four well resolved peaks at  $T < T_N$  ( $\sim$ 373K), and coalesces to a singlet above  $T > T_N$ . Several novel features are notable, including the coexistence of the spectra from the paraelectric and antiferroelectric phase in a short temperature regime around 373K, two  $^{17}\text{O}$  sites in the paraelectric phase and the dynamic coalescence of the spectra at 373. The latter is in contrast to earlier NQR results where the coalescence was noted to occur at about 425K. There is a large change in the  $^{17}\text{O}$  isotropic chemical shift at  $T_N$ , indicating that the phase transition must involve a displacive component, and not solely the order-disorder behavior as assumed in general.

First Principles study on the coexistence of magnetism and  
ferroelectricity in  $\text{YMnO}_3$

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Hexagonal  $\text{YMnO}_3$  is one of the rare materials known to be both ferroelectric and magnetic. The occurrence of these two phase transitions in the same compound stimulated the idea of designing new, powerful technological devices. However, the coexistence of magnetism and ferroelectricity has been object of not much theoretical study so far, and in this work we attempt to understand how magnetic and electric polarizations are related to each other at microscopic level, and which conditions have to be fulfilled for the coexistence to be realized. Specifically, we present results for  $\text{YMnO}_3$  (ferroelectric and antiferromagnetic),  $\text{BaTiO}_3$  (ferroelectric and non magnetic), and  $\text{CaMnO}_3$  (non ferroelectric and antiferromagnetic). Our study reveals the fundamental role of the hybridization between cation d and oxygen p orbitals in ferroelectrics: a strong change of s-p charge hybridization is always associated (and should be considered the driving force) to ferroelectric distortions. Since changes of hybridization are large for materials with mostly unoccupied d orbitals, the possibility of having magnetic ferroelectrics seems to be ruled out. However, this impediment can be overcome in compounds where the electric polarization is constrained to a specific direction. Indeed, only orbitals oriented along this direction contribute substantially to the ferroelectric distortion, whereas orbitals orthogonal to the distortion do not need to fulfill the d<sup>0</sup>-ness criterion, thus they can carry a net magnetic moment. According to our calculations, these conditions are verified in hexagonal  $\text{YMnO}_3$ : the electric polarization is oriented along the c axis, and a magnetic moment equal to  $3.7 \mu_B$  is calculated on each Mn ion, consistent with a S=2 spin state. Furthermore, we find that non magnetic  $\text{YMnO}_3$  can not be ferroelectric, thus for  $\text{YMnO}_3$  magnetism not only does not prevent, but is also necessary for the ferroelectricity to occur.

# First-principles study of $\text{Pb}_2\text{MgTeO}_6$ perovskites

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$\text{Pb}_2\text{MgTeO}_6$  perovskite, elpasolite, is cubic,  $\text{Fm}\bar{3}\text{m}$ , at high temperature and becomes incommensurately modulated with a rhombohedral,  $R\bar{3}$ , average structure at lower temperatures. Both the cubic and the average structure have been investigated using the density functional theory. Elpasolite is an insulator with a 1.5 eV gap. The electronic band structure is composed of weakly dispersive electronic bands. The peaks in the electronic density of states are assigned to the different atomic and/or molecular orbitals. The ab initio determination of the structure is in good agreement with the experiment. The phonons in  $\Gamma$  are analyzed in terms of group theory and compared with the experiment. The Born effective charges and a phonon band structure are also reported.

**Why is there an isotope effect on  $T_c$  in  $\text{KH}_2\text{PO}_4$  upon deuteration but not when replacing  $^{16}\text{O}$  by  $^{18}\text{O}$ ?**

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High-precision NMR experiments on  $\text{KH}_2\text{PO}_4$  (KDP) crystals and its analogues have revealed that the ferroelectric phase transition observed in the KDP-family carries a pronounced displacive component, quite opposite to the general believe that this transition is a prototypical order-disorder driven transition. In consensus with former work the huge isotope effect on  $T_c$  upon deuteration has been confirmed and it was observed that also the deuterated compound shows clear evidence that a coexistence of order-disorder and displacive dynamics are present. Most interestingly oxygen isotope experiments have not been carried through yet to search for an isotope effect on  $T_c$  stemming from the oxygen. Especially the recent finding of oxygen isotope induced ferroelectricity in  $\text{SrTiO}_3$  could have lead to speculate that a pronounced enhancement of  $T_c$  should also be detected in KDP. Yet opposite to these assumptions recent new  $^{18}\text{O}$  NMR measurements on KDP revealed that an isotope effect on  $T_c$  practically does not exist. This finding can be explained within a coupled pseudospin-lattice-electron model, and supports strongly our previous findings of coexistence of order-disorder and displacive dynamics in hydrogen-bonded systems. In addition it is shown, why different results are obtained in the quantum paraelectric  $\text{SrTiO}_3$ , but should not be observable in the analogous compound  $\text{KTaO}_3$ .

# **MODEL OF POLAR CLUSTERS IN RELAXORS : CHARGE TRANSFER AND LOCAL CONFIGURATION INSTABILITY EFFECTS**

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A model of polar clusters (PC) and of chemical fluctuation clusters (CFC) in PMN-like relaxors is proposed. The model is mainly based on the following phenomena. First is a charge transfer state formation corresponded to (i) localized Charge Transfer Vibronic Excitons [1-4] induced by Mg-Nb disorder on the one hand, and to (ii) electronic and hole polaron appearing due to local charge compensation in CFC on the other. Second is Local Configuration Instability phenomenon which is realized in relaxors both in the cases of electronic Jahn-Teller polaron states as well as of cluster ordering states. Local Configuration Instability effects lead to (iii) crossover between small and intermediate electronic polaron states in CFC regions, to (iv) Charge Transfer Vibronic Exciton local ordering [1-3] in PC, and to (v) antiferrodistortive local transformation in CFC. The origin of co-operative phenomena, of Giant Piezoelectric Effect (GPE), and of characteristic dielectric losses including Vogel-Fulcher law validity in relaxors finds possible explanation on the basis of microscopic approach. For instance, GPE is induced by an appearance of mixed TA - soft TO lattice modes as well as of mixed CFC soft antiferrodistortive, and PC soft polar quasilocal modes in the vicinity of PC due to giving rise a strong local piezo-electric effect. Here two addition cross-type lattice-cluster mixed modes are also active in the GPE formation. The drastic increasing of local piezo-electric effect due to the contribution of the soft antiferrodistortive quasilocal CFC mode is induced by the proximity to the Local Configuration Instability point. Recent experimental results of Anomalous Synchrotron X-ray Scattering (A. Tkachuk, H. Chen, P. Zschack, and E. Colla, 2000), of EPR (N. Takesue, Y. Fujii, K. Koyama, M. Motokawa, and H. You, 2000), and of NMR (R. Blinc et al, 1999 – 2000) investigations can be also explained within the model proposed.

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## **Pressure as a Probe of Ferroelectric Properties: Quantum Regime\***

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Quantum fluctuations can strongly influence the low temperature response of a system near a structural phase transition. Among the manifestations of quantum fluctuations at ferroelectric phase transitions are different critical exponents, the suppression of the transition temperature,  $T_c$ , below its classical value and the ultimate development of a quantum paraelectric state. To study these quantum effects as well as the crossover from the classical to the quantum regime, it is necessary to shift  $T_c$  continuously from high to low temperatures. This is conventionally done by chemical substitution, but high pressure is a "cleaner" variable. Results on  $ABO_3$  perovskites exhibiting normal ferroelectric and relaxor behavior at 1 bar will illustrate the above quantum effects at high pressure. Emphasis will be on  $KTaO_3$  and KTN crystals doped with  $\leq 0.05\text{at\%}$  Ca or Ba. The addition of these two dopants introduce dipolar defects into the  $KTaO_3$  lattice which strongly enhance the dielectric susceptibility of the host lattice in the quantum paraelectric state. In a Ca-doped KTN crystal with 2.3at% Nb pressure induces a crossover from normal ferroelectric to a relaxor state which on further increase in pressure crosses over to a quantum paraelectric phase. The susceptibility of the paraelectric phase is very strongly dependent on pressure and biasing electric field. The results will be discussed in terms of the physics involved.

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## **Bound Charge Diffusion and Polar Nanocluster Dynamics in Proton Glass Crystals**

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Slater proposed that  $\text{KH}_2\text{PO}_4$  (KDP) has 2 polar and 4 nonpolar (with higher energy  $E_b$ )  $\text{H}_2\text{PO}_4$  H-bond configurations. Takagi postulated  $\text{H}_3\text{PO}_4$  and  $\text{HPO}_4$  groups with still higher energy  $E_a$ . Via intrabond H transfer, Takagi pairs form, diffuse independently, and recombine or else annihilate with new partners, allowing H-bond reconfiguration. In both KDP-type ferroelectrics and in proton glasses such as  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$  (RADP), at higher temperatures there are many Takagi groups. They have short life and are likely to annihilate with new partners, leading to nearly Debye-like dielectric relaxation. Below the ferroelectric transition in KDP, each Takagi pair member requires energy  $E_b$  to diffuse one step farther from its partner. This energy bias leads to their rapid recombination. In proton glasses with intermediate  $x$ , there is no ferroelectric or antiferroelectric transition. Well above the freezing range, the Takagi concentration falls rapidly with temperature and the Takagi group lifetime and path to annihilation grow long. The energy landscape of the annihilation path must be level on the average. However, the random energy steps  $\pm E_b$  or 0 make the highest barrier encountered be proportional (on average) to the square root of the diffusion path length. As temperature falls, this diffusion inhibition makes recombination more likely than annihilation with new partners. The Takagi pair lifetime becomes shorter, but the fluctuations resulting from their diffusion become biased, so their contribution to dielectric and NMR relaxation weakens. In this same temperature range, the Takagi group population temperature dependence grows weak, because many Takagi groups become stranded, finding no annihilation partner. These stranded groups cause relaxation in their vicinity but no relaxation elsewhere, so the crystal is nonergodic on the time scale concerned. 2D NMR shows the mean (averaged over the crystal) time required for a given nucleus to see a change caused by such diffusion.<sup>1</sup> We propose 4D NMR<sup>2</sup> to test whether this time is different in different crystal nanoregions because of nonergodicity, and to find the time required to restore ergodicity. Another proposed application of 4D NMR is for proton glass crystals with small  $x$ , for which ferroelectric nanoclusters coexist with disordered proton glass regions at low temperatures.<sup>3</sup> We expect that 4D NMR can find the size and lifetime of such polar nanoclusters. Such experiments could also study polar nanocluster size and lifetime in relaxor ferroelectric and related high-piezoelectric-strain crystals.

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## PYROELECTRIC SCANNING MICROSCOPY OF FERROELECTRIC POLYMER FILMS

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We have developed a new technique for imaging the polarization of ferroelectric films and devices-Pyroelectric Scanning Microscopy (PSM). PSM consists of scanning a focused laser beam across a capacitor made of a pyroelectric material. The laser beam is modulated, causing a small modulation in the local film temperature and generating a small ac current due to the pyroelectric effect. Since the pyroelectric current is proportional to the polarization, this technique allows us to image the polarization of the film. Ordinary microscopy affords a resolution of about 1 micrometer while near-field scanning microscopy offers resolutions of 50 nm or better. PSM images of ferroelectric polymer Langmuir-Blodgett films only a few nm thick reveal film inhomogeneities and edge-enhancement effects at intermediate states in the hysteresis loops. The PSM technique can also produce time-resolved movies of dynamic processes like switching by recording switching transients at each image spot and combining the time-space data into image frames, provided that the switching transients are repeatable [1]. The dynamic PS method allows us to monitor inhomogeneity in dynamics and should allow us to record domain motion. See our first Polarization Switching Movie-colored, uncut, and uncensored-at [physics.unl.edu/directory/ducharme/ducharme.html](http://physics.unl.edu/directory/ducharme/ducharme.html).

Work at the University of Nebraska was supported by the USA National Science Foundation, the USA Office of Naval Research, the Nebraska Research Initiative, and the J. A. Woollam Company. Work at the Institute of Crystallography was supported by the Russian Foundation for Basic Research (#99-02-16484) and the Inco-Copernicus Programme (#IC15-CT96-0744).

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# Poster Abstracts

### ***Characterising high-pressure phase transitions by X-ray Diffraction.***

R.J. Angel, N.L. Ross (*Crystallography Laboratory, Dept. Geological Sciences, Virginia Tech, Blacksburg, VA 24060, USA*).

While structural phase transitions as a function of temperature have been studied extensively, relatively little work has been performed at high pressures. The application of pressure to such systems is expected to strongly renormalise the order parameter behaviour and to suppress any dynamic behaviour associated either with intermediate "flip mode" phases or the high-temperature para phases. In addition, pressure couples linearly with the strain in the expression of the free energy of the solid, through the PV term. Thus, unlike temperature, pressure can drive transitions directly through the strain, or by inducing changes in the elastic constants.

Recent advances in the experimental techniques for single-crystal high-pressure X-ray diffraction now allow lattice parameters to be determined routinely to a precision of  $\sim 1$  part in 40,000. The use of internal diffraction standards to measure pressure yields a precision in pressure measurement of better than 0.01 GPa over the pressure range of 0-10 GPa. These advances therefore open up the opportunity of characterising structural phase transitions at high pressures through the determination of the evolution of the spontaneous strain accompanying the transition. Because the coupling of the spontaneous strain to the primary order parameter of the phase transition is governed by symmetry rules, lattice parameter measurements can reveal the order parameter behaviour of the system. Examples of recent work on high-pressure phase transitions in titanites, melilites and lead phosphate will be presented.

## Nonexponential Response in Piezoelectric PVDF

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Polymers are known for displaying nonexponential response to both electrical and mechanical stresses. A numerical method for integrating fractional differential equations has made it possible to verify the connection between a power-law *ac* permittivity function and power-law decay currents resulting from application of a *dc* step voltage. The response shows significant dependence on the duration of the applied pulse. The history dependence predicted by the simulations has been confirmed experimentally. The computational techniques should be applicable to a wide range of systems exhibiting nonexponential response.

## **Computer Simulations of Domain Patterns in Ferroelectrics**

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We study domain pattern formation in ferroelectrics based on a 2-D time-dependent Ginzburg Landau theory. The electrostrictive and elastic effects are included in the form of nonlocal long-range interactions of the polarization field, i.e., by eliminating the strain variables subject to the elastic compatibility constraints. The 2-D system under study has a square to rectangle symmetry change during the paraelectric to ferroelectric phase transition, which creates four equivalent polarization states in the ferroelectric phase. We start the simulation from a paraelectric state that is quenched below the phase transition temperature. Domain pattern evolutions are obtained in absence of external electric field from random field initiated nucleation. In our model, the depolarization field is assumed to be completely screened by surface charges. For the case without defects, the final domain patterns are twinned with only head to tail (uncharged) domain walls. However, for the case with randomly distributed dipolar defects, head-to-head and tail-to-tail charged walls are also observed. These results are in accordance with recent experiments on PMN-PT and PZN-PT domain engineered single crystals, for which charged domain walls have been reported.

**First-Principles Effective Hamiltonians for  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$**

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$\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (PSN) is a relaxor ferroelectric whose dielectric properties depend on the amount of fcc-type ordering of Sc and Nb on the perovskite B-site sublattice. We develop first-principles-based effective Hamiltonians for comparing the temperature-dependent dielectric behavior of ordered and disordered PSN. We compare the virtual crystal approach to modeling arbitrary cation configurations with the supercell approach, the latter based on explicit calculations for differently-ordered hypothetical PSN structures. We determine the sensitivities of ionic effective charges and interatomic forces to their environments and identify which characteristics are transferable between PSN structures with different cation configurations.

## **Multiple Aging Phenomena in Relaxor Ferroelectrics**

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The similarity of many macroscopic properties of relaxor ferroelectrics and spin glasses has led to consideration of the possibility of a close analogy between the collective frozen spin-glass state and a collective frozen state of interacting polar nanodomains. One key signature of spin glass states is a set of peculiar aging effects on the susceptibility  $\chi$ . We present the results of aging experiments on three familiar relaxors: PMN, PLZT 9/65/35 and  $(\text{PMN})_{0.7}(\text{PT})_{0.3}$ . These all show decreases in  $\chi'$  and  $\chi''$  as the sample ages over broad ranges of  $T$ . For PMN, qualitative aging results resembled those for spin glasses. So did the PLZT aging well below the freezing temperature,  $T_g$ . However, PLZT aging near  $T_g$  was dominated by other large effects. PMN-PT aging lacked qualitative memory effects found in spin glasses, resembling instead dirty ferromagnets. Even in PMN, the effective field scale required to erase memory of aging was much larger than the analogous scale in spin glasses. We have preliminary Barkhausen noise results on PMN, which, together with the aging, should help resolve the roles of collective inter-nanodomain structures and random fields in setting the field sensitivity of the aging.

Electron-Nuclear Resonance Spectroscopic Evidence for Defect Pinning of Microdomains in Ferroelectrics: Effect of Charge and Site Substitution

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It has been well-established that defect-related charge imbalance and bonding effects play a significant role in controlling essentially all the properties of ferroelectric crystals and their ceramics and glasses. However, the details of the underlying mechanism at the atomic level are not yet fully understood. With the view of obtaining such details, we have carried out a systematic NMR and EPR study of this phenomenon, starting with the  $\text{KH}_2\text{PO}_4$  (KDP) family. We have introduced known quantity of structural defects, introduced by doping together with radiation exposure. The introduced defects have different sizes, as well charges, and are substituted at both the cation and anionic sites. Temperature dependence of spectroscopic splittings have been used as dynamic probes of the pinning of the microdomains around the defect. Electric field and isotopic effects on the  $T_c$  have been used to verify the proposed mechanism of the microdomain pinning. The presentation will focus on the experimental details of the defect control, dynamics measurement, as well theoretical models of the observed effects.

## SWITCHING DYNAMICS OF TWO-DIMENSIONAL FERROELECTRIC POLYMER FILMS

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The Ferroelectric films of vinylidene fluoride copolymers show finite-size scaling of the coercive field down to thickness of 15 nm, and switching at the intrinsic coercive field of about 500 MV/m in the 15 nm and thinner films, which are made by Langmuir-Blodgett deposition [1], presumably because nucleation is suppressed [2]. While extrinsic switching in the thicker films can be achieved in 1/10 microsecond with exponential dependence on the switching field [3], intrinsic switching in the ultrathin films, 15 nm and thinner, takes 10s of seconds, with weak dependence on the switching field [4]. We have succeeded in preparing films thinner than 15 nm that switch in microseconds with coercive fields of about 50 MV/m and strong dependence of switching time on switching voltage, presumable due to the introduction of new nucleation processes that are not suppressed by nm thickness. These films switch as quickly as 1 microsecond at about 5 V, making the LB ferroelectric copolymer a promising candidate for low-voltage non-volatile random access memories.

Work at the University of Nebraska was supported by the USA National Science Foundation, the USA Office of Naval Research, the Nebraska Research Initiative, and the J. A. Woollam Company. Work at the Institute of Crystallography was supported by the Russian Foundation for Basic Research (#99-02-16484) and the Inco-Copernicus Programme (#IC15-CT96-0744).

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## NANOSCALE PHENOMENA IN FERROELECTRIC THIN FILMS

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Ferroelectric materials are a subject of intense research as potential candidates for applications in non-volatile ferroelectric random access memories (FeRAM), piezoelectric actuators, infrared detectors, optical switches and as high dielectric constant materials for dynamic random access memories (DRAMs). With current trends on miniaturization, it becomes important that the fundamental aspects of scaling of ferroelectric and piezoelectric properties in these devices be studied thoroughly and its impact on the device reliability accessed. In this talk I will present our results on scaling studies of focused ion beam milled submicron ferroelectric capacitors using a variety of scanning probe characterization tools.

In addition to scaling, retention of the logic state in FeRAMs needs further study. In an attempt to understand the nanoscale origins of back-switching of ferroelectric domains, we have examined the time dependent relaxation of remnant polarization in epitaxial lead zirconate titanate ( $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ , PZT) ferroelectric thin films (used as a model system), containing a uniform 2-dimensional grid of  $90^\circ$  domains ( $c$ -axis in the plane of the film) using voltage modulated scanning force microscopy. Relaxation occurs through the nucleation and growth of reverse domains, which subsequently coalesce and consume the entire region as a function of time. Results on the effect of local curvature, faceting, and pinning of  $180^\circ$  domain walls on relaxation kinetics will be presented. This work is supported by National Science Foundation – Materials Research Science and Engineering Center (NSF-MRSEC).

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## Ferroelectric Domains at Nanoscale

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Investigation of nanoscale properties of ferroelectric materials, particularly in a thin layer form, is currently of great interest due to the development of a new generation of electronic devices. One of the most important issues in the physics of ferroelectrics is the formation and evolution of complex domain configurations. Direct imaging of domain structures in thin films and investigation of their behaviour under an applied electric field is essential, since it can provide a clue for general understanding of polarization reversal phenomena and degradation effects in ferroelectric films.

Recently, it was shown that scanning force microscopy (SFM) is a well-suited technique both for nanoscale imaging and control of ferroelectric domains. The SFM imaging method is based on the detection of the piezoelectric vibration of the ferroelectric film excited by an external ac voltage applied through the metallized tip. We demonstrate that application of SFM can successfully address questions of both dynamic and static behavior of domains and domain walls. Ferroelectric domains as small as 20 nm in diameter can be successfully controlled in SFM. This technique provides unique information on basic mechanisms of polarization decay and fatigue in ferroelectric thin films, point-to-point recording of hysteresis loops at the nanometer scale, measurement of transient response during nanoscale ferroelectric switching as well as mapping of leakage current sites.

## **First-Principles and semi-empirical calculations of Atomic and electronic structure for SrTiO<sub>3</sub> (100) and (110) Surfaces**

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We present and discuss results of the calculations of the surface relaxation for SrTiO<sub>3</sub> surfaces with different terminations using a wide variety of methods of computational physics, such as *shell model* as well as *ab initio* methods based on HF and DFT formalism. By means of semi-empirical shell model, the positions of atoms in 16 near-surface layers placed atop a slab of rigid ions are optimized. This permits us determination of a surface rumpling and surface-induced dipole moments (polarization) for different terminations of the (100) and (110) surfaces. Simultaneously, we performed *ab initio* calculations employing as Hartree-Fock, so several different DFT and hybrid techniques. Our shell model results for the (100) surfaces are in good agreement with both our *ab initio* calculations and LEED experiments. For the (110) SrTiO<sub>3</sub> surfaces O-termination is predicted to be the lowest in energy.

## Properties of PZT 95/5 from first principles

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Eric Cockayne, National Institute of Standards

The solid solution  $\text{Pb Zr}_{0.95} \text{Ti}_{0.05}$  (PZT 95/5) undergoes antiferroelectric to ferroelectric phase transition when temperature and pressure vary. This material is therefore useful in many technological applications such as power supply. Since large single crystal samples for the material are not readily available, first principles results are particularly valuable. We investigate various stable and metastable phases of both PZT 95/5 and PZ from first principles, in the LDA approximation, using pseudopotentials. The virtual crystal approximation is applied to treat the solid solution. The zero temperature structure for PZ obtained from first principles is compared to recent X-ray and neutron-scattering experiments. Properties such as polarization and the elastic tensor in various phases are computed. A modified ab initio statistical mechanical Hamiltonian is constructed from the potential energy surface of PZT 95/5, and the zero temperature structures obtained therefrom are compared to the ab initio structures. We also make a comparative study of the energetics and structures in several phases computed using different types of pseudopotentials.

This work was supported by the Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy.

## Virtual Crystal Approximation Study of Monoclinic PZT

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Recently, a new monoclinic phase (space group  $\{Cm\}$ ) of  $Pb(Zr_{1-x}Ti_x)O_3$  (PZT) has been experimentally determined at low temperatures for compositions between  $x=0.45$  and  $x=0.5$  [1]. It has been suggested [2] that this phase may explain the large electromechanical response found in PZT ceramics at these same compositions, since its location in the phase diagram is adjacent to the low-temperature rhombohedral ( $\{R3m\}$ ), high-temperature rhombohedral ( $\{R3c\}$ ) and tetragonal ( $\{P4mm\}$ ) phases.

In this study, we use a first-principles virtual crystal approximation approach [3] to study these four phases in PZT for compositions between  $x=0.4$  and  $x=0.55$ . We determine the energy differences between these phases and construct a theoretical phase diagram at low temperatures which can be compared to the experimentally-determined diagram.

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# Molecular Dynamic Simulations of $\text{MgSiO}_3$ Perovskite and the Composition of the Lower Mantle

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Orthorhombic ( $\text{Pbnm}$ )  $(\text{Mg,Fe})\text{SiO}_3$  perovskite accounts for perhaps two-thirds of the volume of the Earth's lower mantle, so an understanding of its thermal equation of state (EoS) and thermoelastic properties is vital for our understanding of this region. Static compression experiments, however, have covered only the upper third of the lower mantle's geothermal gradient and elastic wave velocity measurements have only been carried out at pressures of up to a few GPa and temperatures  $< 1000$  K. Using molecular dynamics simulations at pressures and temperatures of the lower mantle, we investigated the EoS and elasticity of  $\text{MgSiO}_3$  perovskite. The simulations were done using the non-empirical VIB interatomic potential. This is a many-body potential obtained by overlapping spherical ions. Nominally charged ions give semi-quantitative, but less accurate results than desired for  $\text{MgSiO}_3$  perovskite. By varying the ionic charges, we found it possible to obtain excellent agreement with the much more computationally intensive first-principles LAPW method.

Our P-V-T results were fitted to a thermal EoS of the form  $P(V,T) = P_0(V,T_0) + \Delta P_{th}(T)$ , where  $T_0 = 300$  K and  $P_0$  is the isothermal Universal EoS [Vinet et al., 1987]. The thermal pressure  $\Delta P_{th}$  can be represented by a linear relationship  $\Delta P_{th} = a + bT$  [Anderson, 1980]. Using data calculated at pressures of 0-140 GPa and temperatures of 300-3000 K, we find  $V_0 = 165.40 \text{ \AA}^3$ ,  $KT_0 = 273$  GPa,  $K'T_0 = 3.86$ ,  $a = -1.99$  GPa, and  $b = 0.00664$  GPa/K. Elastic constants were calculated via the lattice fluctuation formula of Parrinello and Rahman [1982]. Calculations at 300 K and 0 GPa give  $KT = 269$  GPa and  $\mu = 159$  GPa, within 2% and 10%, respectively, of the experimentally derived values of 264 and 177 GPa of Yeganeh-Haeri [1994] and in excellent agreement with P-V-T EoS value of 273 GPa. Results for  $KT$  at temperatures of 1000-3000 K and pressures of 25-140 GPa agree within 0.1-5% with values obtained via our P-V-T EoS.

By fixing  $V_0$  to the experimentally determined value of  $162.49 \text{ \AA}^3$  [Mao et al., 1991] and calculating density and seismic velocity profiles along a lower mantle geothermal gradient, we find that the lower mantle cannot consist solely of  $(\text{Mg,Fe})\text{SiO}_3$  perovskite with  $X_{\text{Mg}}$  ranging from 0.9-1.0. Using simplified pyrolytic compositions of 67 mol% perovskite ( $X_{\text{Mg}} = 0.93$ -0.96) and 33 mol% magnesiowustite  $[(\text{Mg,Fe})\text{O}]$  ( $X_{\text{Mg}} = 0.82$ -0.86), however, we obtained density and velocity profiles that are in excellent agreement with seismological models.

## Growth and control of Domain Structure of epitaxial $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ films grown on vicinal (001) $\text{SrTiO}_3$

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Highly tetragonal, epitaxial PZT films with a nominal composition of  $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  exhibit a 2-dimensional grid of  $90^\circ$  domains (*a*-domains, i.e., c-axis in the plane of the film). Our previous studies have revealed that the  $90^\circ$  domains are preferential sites for the nucleation of  $180^\circ$  reverse domains during polarization switching and relaxation. Furthermore, we have observed that this array of  $90^\circ$  domains effectively isolate neighboring c-axis oriented regions. Therefore, we are studying approaches to control the spacing and periodicity of the  $90^\circ$  domains. Such self-assembled arrays of periodic domain structures can form the templates for novel memory arrays. In this paper, we report on the use of vicinally cut [along [100], [010], and [110] directions in the substrate plane] single crystal substrates to control the  $90^\circ$  domain formation. Epitaxial thin films have been deposited by pulsed laser deposition onto the vicinal substrates, with epitaxial conducting oxide bottom electrodes (LSCO and SRO). We have been able to control the nucleation of the  $90^\circ$  twins to occur preferentially at the steps on the substrate. We show that the orientation of these domains can be controlled such that they exhibit only 2 of the 4 possible variants. By using 4-circle x-ray diffraction, TEM and Electric Force Microscopy (EFM) we have investigated the structural and electrical properties of these artificially engineered structures. The control of such structures as a function of film thickness and substrate miscut orientation will be presented.

## Coexisting electronic and magnetic order in dense oxygen

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Using density functional theory within the local spin-density approximation (LSDA) and also with gradient corrections, a new insulating phase of dense oxygen is found to be favored between 10 and 65 GPa, a pressure range coinciding with that of the previously unidentified  $\epsilon$ -phase. Most strikingly, this phase is both antiferromagnetic and antiferroelectric. The phase has an orthorhombic 4-molecule unit cell with space group  $Cmcm$  and is lower in enthalpy than both  $Fmmm$  (ascribed to the  $\delta$ -phase) and  $C2mm$  (proposed for the  $\zeta$ -phase). In addition, a small monoclinic distortion of  $Cmcm$  also appears to be energetically favorable. The existence of antiferroelectricity may explain the pronounced increase in IR activity observed in the  $\epsilon$ -phase.

## Pseudopotential Tail Norm Conservation for Ferroelectric Modeling

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Ferroelectric phenomena result from the interplay of atomic size and atomic polarizability. Therefore, it is vital to use pseudopotentials (PSPs) which accurately represent these atomic properties, to insure the accuracy of pseudopotential (PSP) density functional calculations of ferroelectric materials. The preservation of atomic size for the reference configuration has been formulated into our implementation of the virtual crystal approximation [1] and relativistic PSP [2] constructions. However these methods do not insure the preservation of the atomic size as a function of electronic configuration. Therefore we have recently imposed an additional atomic criterion in our PSP constructions. We quantify the atomic size by examining  $\frac{dN_i}{df_j}$  (the change in wave function tail norm  $N$  for an atomic orbital  $i$  as a function of occupation for an atomic orbital  $j$ ). We will show that the preservation of this quantity dramatically affects the accuracy of the resulting structural and elastic properties of materials in solid-state calculations.

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**Ferroelectric and piezoelectric properties in the presence of  
compositionally broken inversion symmetry**

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We have investigated novel ferroelectric perovskite systems in which compositional inversion symmetry is broken [1]. Our method involves the calculation of the density-functional total energy and Berry-phase polarization. Here we extend the previous work by (i) focusing on the piezoelectric response of the triple-cell heterovalent system  $\text{Ba}(\text{Ti}-\delta, \text{Ti}, \text{Ti}+\delta)\text{O}_3$ , and (ii) studying the strength of the symmetry breaking in the double-cell system  $(\text{Ba}, \text{Sr})(\text{Ti}-\delta, \text{Ti}+\delta)\text{O}_3$  with simultaneous *A*-site and *B*-site substitutions. We observe an enhanced piezoelectric response coefficient  $e_{33}$  when increasing the compositional parameter  $\delta$  in the triple-cell system. This enhancement is quite drastic for the metastable minimum, but only modest for the stable minimum, corresponding respectively to the minority and majority wells of the ferroelectric double-well structure. In the double-cell system, we find that the increase in strength of symmetry breaking with the chemical or concentration perturbation is dominated by the term linear in  $\delta$ , in contrast with the  $\delta^3$  dependence found in the triple-cell system. A symmetry-based justification of the dominance of the linear term is provided.

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## Kinetic Monte Carlo Simulations of Crystal Growth in Ferroelectric Materials<sup>†</sup>

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We study the growth process of ferroelectric materials by kinetic Monte Carlo simulations. An electrostatic model with long-range Coulomb interactions [1] is used to model relaxor single crystals. The growth is characterized by thermodynamic processes involving adsorption and evaporation, with solid-on-solid restrictions. A new algorithm is developed in order to simulate growth under such a model, for which existing kinetic Monte Carlo algorithms are inadequate. We study the growth rates and the order structure of the grown crystals as a function of temperature, chemical composition, and growth orientation. Tests of our algorithm on NaCl give good results. We discuss our on-going simulations of the growth processes in PMN-type materials.

<sup>†</sup> Supported by the Office of Naval Research.

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Pressure Dependence of the Phase Diagram for PZN/PT and PMN/PT Single Crystals  
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We employ hydrostatic pressure to elucidate the nature of the high-temperature cubic-tetragonal ferroelectric (FE) transition and the lower temperature tetragonal-rhombohedral (T-R) structural transition in single crystals of PZN/9.5%PT and PMN/33%PT, compositions near the morphological phase boundary (MPB). This information provides new insight into the physics of these technologically important mixed-oxide materials. The T-R transition is detected in both dielectric constant and dissipation data for both crystals and exhibits some sample-history-dependent effects. The transition temperature shows a gradual increase with pressure in PZN/PT and disappears at pressures above 10 kbar where the T-R phase boundary meets the FE transition. For PMN/PT the T-R transition temperature is nearly independent of pressure up to 7 kbar.

The FE transition temperature in PZN/PT decreases at  $-4.7$  K/kbar from  $\sim 455$  K at ambient pressure; PMN/PT exhibits a larger pressure dependence of  $-5.3$  K/kbar from  $\sim 420$  K at ambient. More importantly, the nature of the FE transition in PZN/PT changes to a diffuse or relaxor characteristic at pressures above 5 kbar as shown by an increasing frequency dispersion in the dielectric constant maximum temperature. The change in the dynamics of the relaxor transition with pressure can be analyzed by fitting the dielectric constant maximum temperature versus frequency to the Vogel-Fulcher equation. The fitting parameters are an energy barrier and "interaction" temperature: the energy barrier increases with increasing pressure while the "interaction" temperature decreases  $\sim 20\%$  faster with pressure than the dielectric maximum temperature at a fixed frequency. These changes are consistent with an increasing isolation of shrinking nanopol FE domains at higher pressures. In contrast to PZN/PT, no crossover to relaxor behavior is observed in the PMN/PT crystal at pressures up to 20 kbar.

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# NEW POLARONIC-TYPE EXCITONS IN FERROELECTRIC OXIDES: NATURE AND EXPERIMENTAL MANIFESTATION

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Charge Transfer Vibronic Exiton (CTVE) in ferroelectric oxides with mixed ionic-covalent type of chemical bonding are correlated pairs or/and triads of electronic and hole polarons [1,2]. Ferroelectric oxides are good examples of such ionic-covalent bonding cases with rather strong charge transfer and not small vibronic interaction. Ferroelectric oxides  $\text{KTaO}_3$  (KTO),  $\text{KNbO}_3$  (KNO), and solid solutions KTN and SBN - bulk as well as thin film materials will be considered as examples of new type excitons of polaronic type (CTVE). Here a review of recent theoretical and experimental investigations of CTVE is presented.

The important feature of CTVE is the formation of charge transfer which is self-consistent with accompanied lattice distortion. The computations of electronic and distorted lattice structure of CTVE in KTO-crystal was performed on the basis of semi-empirical Hartree-Fock calculations using the intermediate neglect of the differential overlap (INDO) method. We have also used the periodic large unit cell method and have extended the primitive KTO unit cell  $3 \times 3 \times 3$  i. e. 27 times. As a result, the following structure of CTVE was obtained. The CTVE here has a triad structure [2] with rather strong vibronic energy lowering ( $\sim 2,71$  eV). This energy lowering is connected with the appearance of a hole polaron on one oxygen ion which has the displacement 5,2 % towards to the first active Ta-ion where the electronic polaron is partly located. This first Ta-ion has a displacement of 3,1 % towards the active oxygen ion. But the second active Ta-ion, where the electronic polaron is also partly located, has a displacement of 4,5 % with repulsion from the active oxygen ion in contrast to the first one. The final charge distribution on these three Ta-O-Ta ions is follow-ing: the first Ta-ion has + 1,74 total charge, while the second Ta-ion has + 2,12 total charge, and active oxygen ion has - 0,24 total charge. The energy level of the electronic polaron on the two Ta-ions is about  $\sim 0,8$  eV lower than the bottom of the conduction band, and the ener-gy level of the hole polaron on the oxygen ion is about  $\sim 1$  eV higher than the top of valence band of the KTO-crystal. Similar triad structure of CTVE was obtained in KNO [3].

It should be underlined that the energy of a possible electron-hole polaron recombination with CTVE collapse corresponds to a luminescence quanta energy equal to about  $\sim 2.14$  eV. This value is in a good agreement with experimental value of the emission quanta energy of detected in KTO so-called «red luminescence» signal [4]. Moreover, as it was shown in [4], the «red luminescence» signal connects with intrinsic defects and is disappearing under the action of any type of heat treatment. Both these properties are in good agreement with the assumption that «red luminescence» in KTO is the CTVE recombination luminescence. Note also that CTVE trapped by Cr or Ce impurities in SBN (S.Kapphan, Ming Gao, V.S. Vikhnin et al, 2000, and S.Avanesyan, H.Liu, V.S. Vikhnin, 2000), or CTVE trapped by Ca-impurity in  $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$  (S. Kapphan, M. Wierschem, V.S. Vikhnin et al, 2000) can be responsible for uncommon visible range light absorption peak. Supported in part by DAAD.

1. V.S.Vikhnin, *Ferroelectrics*, **199**, 25 (1997); *Z. Phys. Chem.*, **201**, 201 (1997).

2. V.S.Vikhnin, H.Liu, W.Jia, S.Kapphan, R.I.Eglitis, D.Usvyat. *J. Lumin.* **83-84**, 109 (1999).

3. E.A.Kotomin, R.I.Eglitis, G.Borstel. *J.Phys.: Condens. Matter* **12**, L557 (2000).

4. V.S.Vikhnin, S.Eden, M.Aulich, S.Kapphan. *Solid State Comm.* **113**, 455 (2000).

## Charge Transfer Electrostatic Model of Compositional Order in Perovskite Alloys\*

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We use an electrostatic model including charge transfer to study compositional ordering in perovskite alloys with A-site and B-site doping. The method [1] generalizes the approach of Bellaiche and Vanderbilt [2], who used nominal ionic charges. The large covalency of  $\text{Pb}^{2+}$  compared to  $\text{Ba}^{2+}$  is modeled by an environment dependent effective A-site charge. Monte Carlo simulations of this model reproduce the long range compositional order of both Pb-based and Ba-based  $\text{A}(\text{BB}'\text{B}'')\text{O}_3$  perovskite alloys as a function of temperature and  $\text{B}^{4+}$  concentration. In systems with both A- and B-site doping, such as  $(\text{Na}_{1/2}\text{La}_{1/2})(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ ,  $(\text{Ba}_{1-x}\text{La}_x)(\text{Mg}_{(1+x)/3}\text{Nb}_{(2-x)/3})\text{O}_3$  and  $(\text{Pb}_{1-x}\text{La}_x)(\text{Mg}_{(1+x)/3}\text{Ta}_{(2-x)/3})\text{O}_3$  [3], purely electrostatic interactions reproduce general trends, and charge transfer effects indicate that local structural relaxations can tip the balance between different B-site orderings in Pb based materials.

\* Supported by the Office of Naval Research.

[1] M. Wu and H. Krakauer, <http://xxx.lanl.gov/abs/cond-mat/0011063>, to be published.

[2] L. Bellaiche and D. Vanderbilt, Phys. Rev. Lett. **81**, 1318 (1998).

[3] L. Dupont, L. Chai, P.K. Davis, Sol. St. Chem. Inorg. Mater. II **547**, 93-98 (1999); J.K. Montgomery, M.A. Akbas and P.K. Davies. J. Am. Ceram. Soc. **82**, 3481 (1999).

# Final Program Schedule - Feb. 4, 2001

## 2001 Workshop on Fundamental Physics of Ferroelectrics

February 4-7, 2001, Williamsburg, VA, USA

Sun Feb 4	5:00 PM	7:00 PM	REGISTRATION	CASCADES FOYER
	5:30 PM	7:00 PM	RECEPTION	COUNCIL ROOM
	7:00 PM		DINNER	COUNCIL ROOM
Mon Feb 5	8:00 AM	8:30 AM	REGISTRATION	CASCADES FOYER
			CASCADES ROOM	Session Chair: Henry Krakauer
	8:30 AM	8:40 AM	Opening Remarks	
	8:40 AM	9:15 AM	J. Scott	Polarons and oxygen vacancy clusters in ferroelectric thin films
	9:15 AM	9:50 AM	R. Ramesh	Polarization dynamics in ferroelectric thin films and nanostructures
	9:50 AM	10:15 AM	COFFEE	
	10:15 AM	10:50 AM	D. Vanderbilt	Domain walls and compositional disorder in Pb-based perovskites
	10:50 AM	11:25 AM	R. Cohen	Polarization rotational, elastic, and electromechanical properties of piezoelectrics
	11:25 AM	12:00 PM	D. Singh	Lattice distortions in Pb(Zr,Ti)O <sub>3</sub> alloys near the morphotropic phase boundary
	12:00 PM	1:00 PM	LUNCH	CASCADES GARDEN ROOM
			CASCADES ROOM	Session Chair: Ronald Cohen
	1:00 PM	1:35 PM	W. Dmowski	Local atomic structure of PbZrO <sub>3</sub> -PbTiO <sub>3</sub> near the morphotropic phase boundary
	1:35 PM	2:10 PM	H. Chen	Synchrotron X-ray studies of superlattice ordering in lead magnesium niobate single-crystal doped with 6.25% Ti
	2:10 PM	2:45 PM	S. Kojima	Broadband-Brillouin scattering of relaxor ferroelectric crystals
	2:45 PM	3:15 PM	COFFEE	
	3:15 PM	3:50 PM	K. Rabe	Improving effective Hamiltonians for simple and complex ferroelectric systems
	3:50 PM	4:25 PM	L. Bellaiche	Composition modulation in Pb(Sc, Nb)O <sub>3</sub> alloys
	4:25 PM	5:00 PM	K. Bhattacharya	Domain patterns and macroscopic electro-mechanical behavior
	5:00 PM	5:20 PM	GENERAL DISCUSSION	
	6:30 PM	7:30 PM	DINNER	CASCADES GARDEN ROOM
	7:30 PM	9:30 PM	POSTER SESSION	SEMINAR ROOM

## Poster Session, Mon Feb 5, 7:30 PM - 9:30 PM

**R.J. Angel and N.L. Ross**, Characterizing high-pressure phase transitions by X-ray Diffraction ←

**G. W. Bohannon**, Nonexponential Response in Piezoelectric PVDF

**W. Cao and Ahluwalia**, Computer Simulations of Domain Patterns in Ferroelectrics

**E. Cockayne, B. Burton, and L. Bellaiche**, First-principles Effective Hamiltonians for  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  ←

**E. V. Colla, Lambert K. Chao, M. B. Weissman**, Multiple Aging Phenomena in Relaxor Ferroelectrics

**N. Dalal and D. Viehland**, Electron-nuclear resonance spectroscopic evidence for defect pinning of microdomains in ferroelectrics: effect of charge and site substitution ←

**S. Ducharme, T. Reece, A.V. Sorokin, L.M. Blinov, V.M. Fridkin, S.P. Palto, K. Verkhovshaya, N.N. Petukhova, and S.G. Yudin**, Switching dynamics of two-dimensional ferroelectric polymer films

**C.S. Ganpule**, Nanoscale phenomena in ferroelectric thin films

**A. Gruverman**, Ferroelectric domains at nanoscale

**E. Heifets, and R. E. Cohen**, First-Principles and semi-empirical calculations of atomic and electronic structure for  $\text{SrTiO}_3$  (100) and (110) Surfaces

**K. Leung and A. F. Wright**, Properties of PZT 95/5 from first principles ←

**F. C. Marton and R. E. Cohen**, Molecular dynamic simulations of  $\text{MgSiO}_3$  ←

**V. Nagarajan, C. Ganpule, S. P. Alpay, A. Roytburd and R. Ramesh**, Growth and control of domain structure of epitaxial  $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  films grown on vicinal (001)  $\text{SrTiO}_3$ .

**J.B. Neaton and N.W. Ashcroft**, Coexisting electronic and magnetic order in dense oxygen. ←

**N.J. Ramer, I. Grinberg, and A. Rappe**, Pseudopotential tail norm conservation for ferroelectric modeling ←

**N. Sai, B. Meyer, and D. Vanderbilt**, Ferroelectric and piezoelectric properties in the presence of compositionally broken inversion symmetry ←

**M. Suewattana, C. Tahan, P. Larsen, S. Zhang, and H. Krakauer**, Kinetic Monte Carlo simulations of crystal growth in ferroelectric materials

**E.L. Venturini, G.A. Samara, B.A. Tuttle, and V.H. Schmidt**, Pressure Dependence of the Phase Diagram for PZN/PT and PMN/PT Single Crystals ←

**V. S. Vikhnin, R. I. Eglitis, E.A. Kotomin, and S. Kapphan**, New polaronic-type excitons in ferroelectric oxides: nature and experimental manifestation

**Z. Wu and H. Krakauer**, Charge transfer electrostatic model of compositional order in perovskite alloys ←

Tue Feb 6

CASCADES ROOM

8:30 AM 9:05 AM B. Burton

9:05 AM 9:40 AM A. Rappe

9:40 AM 10:10 AM COFFEE

10:10 AM 10:45 AM R. Blinc

10:45 AM 11:20 AM Y. Yacoby

11:20 AM 11:55 AM R. Resta

11:55 AM 1:20 PM LUNCH

CASCADES ROOM

1:20 PM 1:55 PM S. Zhang

1:55 PM 2:30 PM D. Viehland

2:30 PM 3:05 PM N. Dalal

3:05 PM 3:35 PM COFFEE

3:35 PM 4:10 PM A. Filippetti

4:10 PM 4:45 PM R. Caracas

7:00 PM 9:00 PM BANQUET

Session Chair: David Vanderbilt

Cation ordering in  $[\text{Na}_{1/2}\text{Bi}_{1/2}]\text{TiO}_3$  alloys

Geometric formulation of quantum stress fields in density functional theory

Dynamics of relaxors

Ferroelectricity in doped incipient ferroelectrics

What happens inside a polarized dielectric?

CASCADES GARDEN ROOM

Session Chair: Shiwei Zhang

Kinetic Monte Carlo simulations of crystal growth in ferroelectric materials

Importance of quenched-disorder on the structure-property relations of oriented piezocrystals

$^{17}\text{O}$  Isotropic Chemical Shift Probing of Phase Transitions in H-bonded Solids: Squaric Acid

First-Principles study on the coexistence of magnetism and ferroelectricity in  $\text{YMnO}_3$

First-principles study of  $\text{Pb}_2\text{MgTeO}_6$  perovskites

SHIELDS TAVERN, Duke of Gloucester St.

← 1 hour discussion

Wed Feb 7

CASCADES ROOM 2

8:30 AM 9:05 AM A. Bussman-Holder

9:05 AM 9:40 AM V. Vikhnin

9:40 AM 10:10 AM COFFEE

10:10 AM 10:45 AM G. Samara

10:45 AM 11:20 AM H. Schmidt

11:20 AM 11:55 AM S. Ducharme

11:55 AM 1:00 PM LUNCH

Session Chair: Takeshi Egami

Why is there a  $T_c$  isotope effect in  $\text{KH}_2\text{PO}_4$  upon deuteration but not when replacing  $^{16}\text{O}$  by  $^{18}\text{O}$ ?

Model of polar clusters in relaxors: charge transfer and local configuration instability effects

Pressure as a probe of ferroelectric properties: quantum regime

Bound charge diffusion and polar nanocluster dynamics in proton glass crystals

Pyroelectric scanning microscopy of ferroelectric polymer films

CASCADES GARDEN ROOM

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